Let's Learn
CHEMISTRY
Together

JOHN T. LI

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Table of Contents

Preface

Welcome! You are currently reading Pareto Scientific's first publication! We hope you enjoy the text, and use it to your advantage to refine your knowledge and understanding of chemistry. Since this is the first edition, we especially need your comments, responses, and opinions so that we can adapt this book to fit your needs. We are always open to your intellectual contributions because we believe that we need your support and feedback to continuously develop. If you have any suggestions, please send an email to us, and we will immediately see what we can do for you! (The email is set up, so that if you send to us an email containing the word "chemistry," it will automatically be forwarded to the people who wrote this text)

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About Pareto Scientific

We are a private, independent, multidisciplinary academic organization that creates creative commons resources for students. The group is composed of unconventional partnerships and collaborations between students and mentors who are researchers and authors. We believe that education can be greatly facilitated by students for students. The members of this group consist of people with various backgrounds, and projects can be initiated and led by any member. Pareto Scientific mainly outputs principle-based texts that are not test oriented, because deep understanding of fundamental principles automatically leads to superior academic performance and minimizes student stress. This first book can be used to supplement higher level chemistry courses for deeper study of chemical principles that are often only briefly touched upon, to self-study a select number of ideas in chemistry, to prepare students for tournaments such as the Chemistry Olympiad, or to be used for any purpose that it is found to be helpful!

Why We Wrote This Text

General chemistry is a foundation for further study. Although most courses consist of a mountain of rote calculations, the true purpose of general chemistry is to give a sound foundation for further learning. This book is aimed to help students conceptually and mathematically understand chemistry at a basic level, and mainly covers topics that are not discussed to the

maximum extent in most general chemistry classes. Therefore, it seeks to expand upon the existing knowledge of the student as much as possible. It is recommended to read this text concurrently with a relevant class, as the text is not centered around calculation methods and procedures for taking tests. This means that we will not excessively bore you with calculations. As a principle-based text, it goes straight to the point with derivations and explanations.

This book is in no way a substitute for the usual general chemistry textbook. Rather, it is a very basic theoretical chemistry textbook which draws its topics and approaches from many sources of varying difficulty. With all said, it is time to do. At each and every step, make sure you understand what you read. History is included, in order to highlight important experiments and discoveries. Thus, most chapters are broken down into two sections. The first section covers important principles along with historical background, and the second section usually involves rigorous proofs of the ideas contained inside of the first section. Some of the proofs need some understanding of calculus to understand, and for most basic courses they can be skipped. However, if you can understand the mathematics used, it is recommended that you follow the proofs through, because deeper understanding is rooted in investigating how each of the classical equations work. All sections that require an understanding of calculus have the integral signs $\iiint$ in the top right corner. If you ever get stuck, or feel like you don't understand something, read it again and supplement your knowledge with other sources. If you think something is wrong (as humans we are all fallible), just email us. We will make sure to answer you to the best of our ability!

Chapter 1: Basics

The Standard International System of Measurement

Base Units

The Standard International (SI) metric system has seven base units.

SI Base Units			
Quantity	Quantity Symbol	SI Base Unit	Unit Symbol
Length, distance	*l, h, r*	Meter	m
Mass	*m*	Kilogram	kg
Time	*t*	Second	s
Electric Current	*I, i*	Ampere	A
Thermodynamic Absolute Temperature	*T*	Kelvin	K
Amount of substance	*n*	Mole	mol
Luminous Intensity	I_v	Candela	cd

Since physicists decided on the system, the base unit for mass is the kilogram. However, in chemistry, we most often use grams, because we are working with far smaller amounts of substance.

Derived Units

All other units, such as the joule and the newton, are called derived units because they can be expressed as combinations of the seven base units.

Quantity	Common Symbols	Unit Name	Derived unit
Energy	*U, E, K*	joule	$1\text{kg} * \text{m}^2/\text{s}^2 = 1$ joule

Scaling Prefixes

Any unit can be multiplied by powers of ten in order to scale it up or down to useful size. To change the scale of a unit, we simply add a prefix to the unit. Common prefixes are in the table below.

Scale	Prefix	Abbreviation
10^{12}	Tera-	T
10^{9}	Giga-	G
10^{6}	Mega-	M
10^{3}	kilo-	k
10^{2}	hecto-	h
10	deca-	dK or da
1		
10^{-1}	deci-	d
10^{-2}	centi-	c
10^{-3}	mili-	m
10^{-6}	micro-	μ
10^{-9}	nano-	n
10^{-12}	pico-	p
10^{-15}	femto-	f

Dimensional Analysis

In chemistry, we nearly exclusively use the SI metric system. However, sometimes we will need to keep track of units during conversions and calculations. We do so by performing a

process called dimensional analysis. Converting by dimensional analysis works by multiplying each value by a form of 1, called a conversion factor. For example, observe the following:

$$1 \text{ meter} \left(\frac{100 \text{ centimeters}}{1 \text{ meter}} \right) = 100 \text{ Centimeters}$$

Note how the meter was divided out, and centimeters remain. We know we multiplied by 1, because 100 centimeters has the same length as 1 meter. The fraction is the conversion factor in this case. The same applies for more complex units. For example, the SI unit for energy, the joule, is equal to

$$1 \text{ J} = 1 \text{ kg} \frac{\text{m}^2}{\text{s}^2}$$

Conversion Factors

If we want to convert one joule to calories, which is the amount of energy required to warm 1 gram of water by 1 degree Celsius, then we use the appropriate conversion factor. Conversion factors are always equal to 1, and for any situation, two conversion factors may be given. The two will always be inverses, because dividing 1 by 1 always equals 1, regardless of the order of division.

$$1 = \frac{0.239 \text{ calories}}{1 \text{ joule}} = \frac{4.184 \text{ joules}}{1 \text{ calorie}}$$

In order to convert from one unit to the other, you have to multiply or divide depending upon what you are given. For example, we can be asked to do four types of tasks based upon what was given:

Convert 5 joules to calories, given $\frac{0.239 \text{ calories}}{1 \text{ joule}}$

$$(5 \text{ joules}) \left(\frac{0.239 \text{ calories}}{1 \text{ joule}} \right) = 1.195 \text{ calories}$$

Convert 5 joules to calories, given $\frac{4.184 \text{ joules}}{1 \text{ calorie}}$

Chapter 1: Basics

$$(5 \text{ joules})/\left(\frac{4.184 \text{ joules}}{1 \text{ calorie}}\right) = (5 \text{ joules})\left(\frac{1 \text{ calorie}}{4.184 \text{ joules}}\right) = 1.195 \text{ calories}$$

Convert 3 calories to joules, given $\frac{4.184 \text{ joules}}{1 \text{ calorie}}$

$$(3 \text{ calories})\left(\frac{4.184 \text{ joules}}{1 \text{ calorie}}\right) = 12.552 \text{ joules}$$

Convert 3 calories to joules, given $\frac{0.239 \text{ calories}}{1 \text{ joule}}$

$$(3 \text{ calories})/\left(\frac{0.239 \text{ calories}}{1 \text{ joule}}\right) = (3 \text{ calories})\left(\frac{1 \text{ joule}}{2.39 \text{ calories}}\right) = 12.552 \text{ joules}$$

Example:

Notice that whenever we convert, we divide out and cancel the original unit, and multiply by the new unit. However, questions don't stay this easy, especially if you get something like:

Convert $300\frac{km}{s^2}$ into $\frac{inches}{hr^2}$, given that:

$$1 \text{ km} = 1000 \text{ m}, 1 \text{ foot} = 304.8 \text{ mm}, 1000 \text{ mm} = 1 \text{ m}, 60 \text{ minutes} = 1 \text{ hour},$$
$$60 \text{ seconds} = 1 \text{ minute, and } 1 \text{ foot} = 12 \text{ inches}$$

This is when you are supposed to really analyze the "dimensions." After some head scratching, we come up with:

$$\left(300\frac{km}{s^2}\right)\left(\frac{1000m}{km}\right) = 300000\frac{m}{s^2}$$

$$\left(300000\frac{m}{s^2}\right)\left(\frac{1000 \text{ mm}}{m}\right) = 300000000\frac{mm}{s^2}$$

$$\left(300000000\frac{mm}{s^2}\right)\left(\frac{1 \text{ ft}}{304.8 \text{ mm}}\right) = 984251.969\frac{ft}{s^2}$$

$$\left(984251.969\frac{ft}{s^2}\right)\left(12\frac{in}{ft}\right) = 11811023.6\frac{in}{s^2}$$

$$\left(11811023.6\frac{in}{s^2}\right)\left(\frac{60 \text{ s}}{1 \text{ min}}\right) = 708661416\frac{in}{s * min}$$

4

$$\left(708661416\,\frac{\text{in}}{\text{s} * \text{min}}\right)\left(\frac{60\text{ s}}{1\text{ min}}\right) = 42519684960\,\frac{\text{in}}{\text{min}^2}$$

$$\left(42519684960\,\frac{\text{in}}{\text{min}^2}\right)\left(\frac{60\text{ min}}{\text{hr}}\right) = 2.5511811\text{x}10^{12}\,\frac{\text{in}}{\text{min} * \text{hr}}$$

$$\left(2.5511811\text{x}10^{12}\,\frac{\text{in}}{\text{min} * \text{hr}}\right)\left(\frac{60\text{ min}}{\text{hr}}\right) = 1.5307087\text{x}10^{14}\,\frac{\text{in}}{\text{hr}^2}$$

Crazy, eh? Yeah, it's just a bunch of boring calculations. You can multiply all the conversion factors together, and then multiply by the initial value. Thus, multiplying 300 km/s^2 by:

$\dfrac{5.1023622\text{x}10^{11}\frac{\text{in}}{\text{hr}^2}}{1\frac{\text{km}}{\text{s}^2}}$ yields the same result, because multiplication is commutative and associative.

That is just a preference, and eventually you will do whatever you feel comfortable doing anyways, as long as you get the correct result!

Another Example:

Convert 2.000 joules into $\frac{\text{g} * \text{cm}^2}{\text{hr}^2}$. So, we do the following:

$$(2.000\text{ J})\left(\frac{1\frac{\text{kg} * \text{m}^2}{\text{s}^2}}{1\text{ J}}\right) = 2.000\,\frac{\text{kg} * \text{m}^2}{\text{s}^2}$$

$$\left(2.000\,\frac{\text{kg} * \text{m}^2}{\text{s}^2}\right)\left(\frac{10^3\text{g}}{1\text{ kg}}\right) = 2.000 * 10^3\,\frac{\text{g} * \text{m}^2}{\text{s}^2}$$

$$\left(2.000 * 10^3\,\frac{\text{g} * \text{m}^2}{\text{s}^2}\right)\left(\frac{10^2\text{ cm}}{1\text{ m}}\right) = 2.000 * 10^5\,\frac{\text{g} * \text{m} * \text{cm}}{\text{s}^2}$$

$$\left(2.000 * 10^5\,\frac{\text{g} * \text{m} * \text{cm}}{\text{s}^2}\right)\left(\frac{10^2\text{ cm}}{1\text{ m}}\right) = 2.000 * 10^7\,\frac{\text{g} * \text{cm}^2}{\text{s}^2}$$

$$\left(2.000 * 10^7\,\frac{\text{g} * \text{cm}^2}{\text{s}^2}\right)\left(\frac{3600\text{ s}}{1\text{ hr}}\right) = 7.200 * 10^{10}\,\frac{\text{g} * \text{cm}^2}{\text{s} * \text{hr}}$$

$$\left(7.200 * 10^{10}\,\frac{\text{g} * \text{cm}^2}{\text{s} * \text{hr}}\right)\left(\frac{3600\text{ s}}{1\text{ hr}}\right) = 2.592 * 10^{14}\,\frac{\text{g} * \text{cm}^2}{\text{hr}^2}$$

Likewise, multiplying 2.000 joules by

Chapter 1: Basics

$$\left(\dfrac{1\,\frac{\text{kg} * \text{m}^2}{\text{s}^2}}{1\,\text{J}} \right) \left(\dfrac{10^3\text{g}}{1\,\text{kg}} \right) \left(\dfrac{10^2\,\text{cm}}{1\,\text{m}} \right)^2 \left(\dfrac{3600\,\text{s}}{1\,\text{hr}} \right)^2$$

yields the same result, because multiplication is commutative and associative.

When performing complex calculations, be sure to keep the units, because they help make sure that you do not mix the numbers and get the wrong answer. If the question is asking for an amount of time, an answer in kilograms is obviously wrong. The second you notice something like that, you should immediately check your work, because most likely one of the conversions has gone wrong.

Significant Figures

Another calculation topic is significant figures. Significant figures indicate the precision of numbers. There is a difference between precise and accurate. Accurate means that the average of the numbers obtained from an experiment is close to the actual value. Precise means that the numbers obtained from an experiment are close to each other. In experiments, you want to be accurate and precise. Usually, with reasonably good equipment, precision should not be a problem. However, accuracy is often low due to improper calibration of the equipment, or human error. Significant figures tell us something about the precision. To improve precision, we need more accurate instruments and superior quality control. However, only results from multiple trials against a reference standard tells us something about the accuracy. Therefore, to improve accuracy, it is recommended to perform multiple trials of an experiment, and have something to compare those trials to.

Significant figures are written as follows: you write all the digits of the number, up until the first digit that you are uncertain about. All the digits of a number, up until the first estimated digit are significant figures. Then, if you want to, all digits past the last significant figure can be written as a subscript under the number. Good experiments usually have less than 1 percent error, and excellent experiments generally have close to no error. Beakers generally have a large amount of error, and should NEVER be used to measuring volumes. Pipettes and graduated cylinders should be used instead. For example, let's say that I am making the mistake of using a

beaker, which has an accuracy of ±5%. Thus, in this case, if I measured 95.75 milliliters, I would write 95.$_7$ mL, or just 96 mL. Thus, we write all the digits that we are fairly certain about, which is the 9, and write one additional digit, which is, in a sense, "guessed". We find that using that beaker just destroyed any possibility of obtaining accurate results. If we are massing on a scale which can measure up to an accuracy of 0.001 gram, and we measure out 5.23512 grams, then we would write 5.2351$_2$ grams, or just 5.2351 grams. When calculating, however, NEVER cut off any of the digits on the end of the numbers! Cutting off these "guard digits" leads to large errors, especially if you cut them off at every step of the calculation. Only round once, when you are giving your final answer.

Addition and Subtraction

When performing a calculation, there are some rules about the number of significant figures. For example, when adding or subtracting, the last significant figure is to the place value of the last significant figure of the number that has the least precision. Thus, if I do 123.6$_2$ - 45.123124413$_4$, my result, to the last significant figure, would be 78.4$_9$, or just 78.5, because the error in the first number greatly overwhelms the precision of the second number. No matter how precise the second number is, the error will not be smaller than the last significant digit of the first number. Here are some more examples:

$$3123.0 - 2132.468 = 990.5_{32}, \text{which can be rounded to } 990.5$$

Note that the zero, if it is after the decimal point, counts as a significant figure. However, if we do:

$$32000 - 1625 = 30_{375}$$

The answer in proper significant figures is $3.0 * 10^4$, which has only two significant figures because the last significant figure of the 32000 is the 2. All trailing zeros that are not followed by or preceded by a decimal point are not significant figures. Thus, if there are no decimal places, the last significant figure is the one which there are only zeros after.

Thus:

$$32000.0 + 1625 = 3362_5$$

7

And the answer to proper significant figures is 33630.

Whereas

$$32000 + 1625 = 33_{625}$$

And the answer to proper significant figures is 34000

Something that we must watch out for, is units. If one of the numbers is 50.01 kg, and the other number is 1.0 g, adding the two results in 50.011 kg. However, if we follow significant figures, the 50.01 kg can be rewritten as 50010 g, whose last significant figure is the tens digit. Thus, adding the two results in 50010 kg when rounded to proper significant figures, because the 1 gram is very likely to be smaller than the error of the initial measurement of the 50.01 kg, and the 1 gram is relatively insignificant.

Multiplication and Division

For multiplication and division, we only keep the same number of significant figures as the least uncertain number. For example:

$$25.0000 \text{x} 5.0 = 12_{5.0}$$

And the answer to correct significant figures is 130

Whereas

$$25.0000 \text{x} 5 = 1_{25.0}$$

And the answer to correct significant figures is 100

For division, the same rules apply:

$$\frac{23.0}{15.00} = 1.53_3$$

And the answer to correct significant figures is 1.53

Chapter 1: Basics

Whereas

$$\frac{23}{15.00} = 1.5_{33}$$

And the answer to correct significant figures is 1.5

Usually, significant figures should be fine, as long as you are not more than one significant figures away. It just is a way of bookkeeping, so that you can know how big of an error to expect.

Mathematical Relationships

Direct Relationship

An increase in one variable results in an increase in the other variable. It is most commonly represented as a line.

$$y = mx, \text{where m is a constant, and x and y are the related variables}$$

Here, y is equal to m times x. Likewise, y divided by m is equal to x. Thus, if x increases, y must increase, and if y increases, x must increase, and vice versa. Therefore, we say that x and y are proportional to each other if there is a constant that relates x and y in the following manner, which indicates a direct relationship. The α indicates proportionality.

$$(x \propto y) \text{ if } xm = y \text{ or likewise } yn = x, \text{where m and n are constants}$$
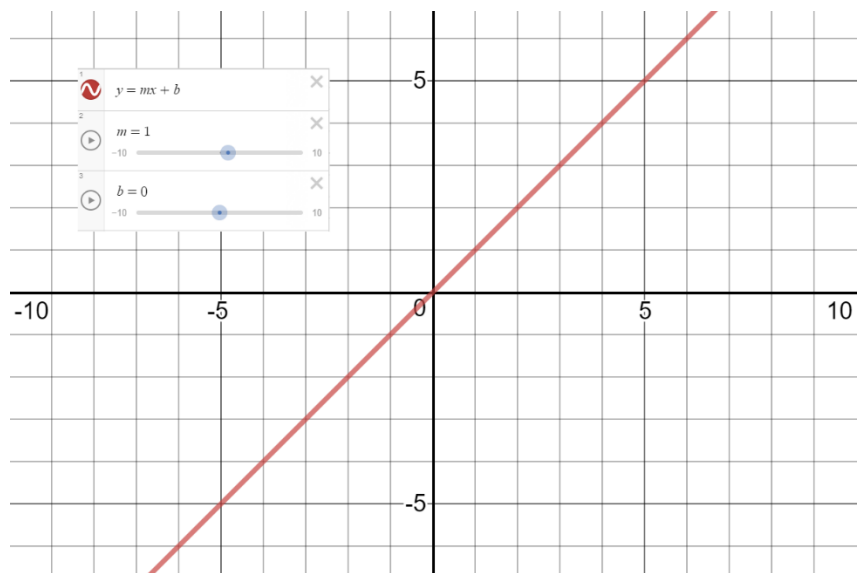
Figure 1.1. Graph of y=mx+b, a line.

Slopes of Graphs of Direct Relationships:

The definition of slope, $\frac{\Delta y}{\Delta x} = $ m, indicates that for a direct relationship, when we divide a change in y due to a change in x, Δy, by that change in x, Δx, we get a constant value, which is the slope of the line from our graph shown above. A line is the only type of function with a constant slope. Therefore, direct relationships can be conveniently plotted as lines. If any two functions, $f(x)$ and $g(x)$, are related as follows:

$$\frac{f(x)}{g(x)} = \text{k, where k a constant}$$

Then plotting the two functions on the x and y axes results in a line. This makes sense, because we get a constant for dividing any change in the value of $f(x)$ by a corresponding change in the value of $g(x)$ if and only if the graph is a line. Rearranging, we get the following:

$$f(x) = kg(x)$$

Which, if we define $f(x) = $ y and $g(x) = $ x, then we arrive at a form of a line.

$$y = \text{kx, where k is a constant slope.}$$

10

Inverse Relationship

An increase in one variable results in a decrease in the other variable.

$$y = \frac{m}{x}, \text{where m is a constant, and x and y are related variables}$$

Since m is a constant, if x increases, y must decrease. This can also be written as follows:

$$x = \frac{m}{y}$$

Thus, if y increases, x must therefore decrease. We can also say that they are inversely proportional, where an increase in y by a factor leads to a corresponding decrease in x by that same factor, and vice versa.
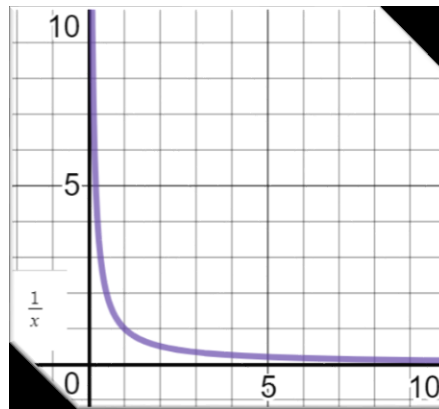
Figure 1.2. Graph of y=1/x.

Inverse Square Relation

For many calculations involving forces, such as the force of gravity or the electromagnetic force, we have an inverse-square relation between the strength of the force and the distance between the two objects that exert the force on each other. Note that we say two objects, because according to Newton's third law, every force exerted on an object must have a complementary force exerted on the complementary object. We can symbolically write it as follows:

$$F = \frac{b}{r^2}, \text{where } F \text{ is the force, b is a constant, and } r \text{ is the distance between the two objects}$$

Chapter 1: Basics
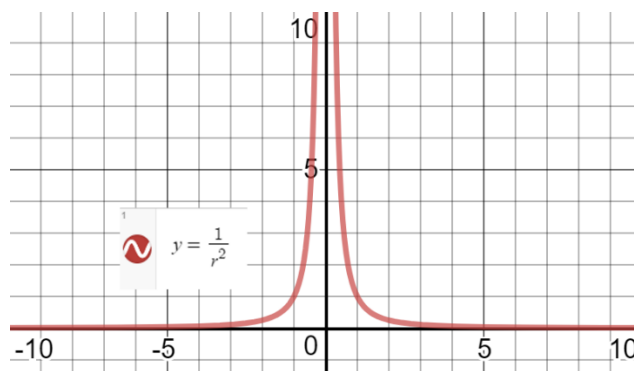
Figure 1.3. Graph of y=1/r^2.

Therefore, we find that tripling the distance between the two objects reduces the strength of the force by 9, because

$$F_{3r} = \frac{b}{(3r)^2} = \frac{b}{(3)^2 r^2} = \frac{b}{9r^2} = \frac{1}{9}F_r$$

Multiplying the distance between the two objects by any factor multiplies the force by the inverse of the square of the factor. Thus, multiplying the distance by n divides the strength of the force by n^2. Inverse square relations are important, especially in chemistry, because nearly all of the interactions between electrons, protons, atoms, and molecules are due to the electromagnetic force, which is an inverse square force.

Summary of Math Needed

A decent amount of math is needed for chemistry. The trick is to either get good at basic arithmetic and algebra, or become a calculator wizard. Here is a list of all the mathematical skills that may be needed:

- Arithmetic (+-x/)
- Using scientific notation
- Algebra (solving for roots of basic polynomials)
- Relationships
- How to plot a line
- Rate of change (slope)

- Logarithms, and exponents
- Guessing and problem solving

Accidental calculation errors and math errors are very common. However, they can be avoided by learning how to calculate everything carefully, because sound calculation techniques save time and ensure accuracy.

Short Summary of the Basics

- We use SI units in chemistry.
- Dimensional analysis is used to inspect the units of the numbers.
- Conversions are done by multiplying or dividing by conversion factors, which are all equal to 1.
- Accuracy is how close the average of many results is to the actual value.
- Precision is how close the results are to each other.
- Significant figures measure precision.
- The last significant figure is the first estimated digit. However, you can write additional insignificant figures. Just make sure they are subscripted, so that others know that the figures are not significant.
- When calculating, do not cut off the end digits. Keep them in your calculator.
- Zeros that are preceded or followed by the decimal point are significant figures.
- If a number does not contain a decimal point, the last significant digit is the last nonzero digit.
- When adding and subtracting, the last significant figure is in the same place value (power of ten) as the place value of the last significant figure of the least precise number.
- When multiplying and dividing, we keep the same number of significant figures as the number with the least number of significant figures.
- Round your final answer to the last significant figure.
- Direct, inverse, and inverse square relations
- Precision in calculations is king. Either get good at math, or become a calculizard (calculator wizard).

Chapter 2: Conservation

Stoichiometry

Most matter is measured on three scales, being the quantum scale, the microscopic scale, and the macroscopic scale. A scale is just a perspective, and when we say that something is on a given scale, we just mean that we can see it when we zoom in to that size. We will touch briefly upon the quantum scale when discussing the atom. Atoms and molecules are observed on the microscopic and quantum scales. As the name suggests, the microscopic scale includes everything that is equal to or smaller than 10^{-6} meters. Atoms are very small, and are about 10^{-10} meters. Since we work with atoms frequently, we have a special unit for 10^{-10} meters, which is called the Angstrom, Å.

$$1\,\text{Å} = 10^{-10}\,\text{m}$$

Because atoms are so small, most of the things that we normally interact with are on the macroscopic scale, being made up of numerous atoms. Thus, we have the concept of a mole. To say that we have a mole of something is just like saying we have a dozen of something. When we say we have a dozen of something, we have 12 of that something. Likewise, when we say we have a mole of something, we are saying that we have an Avogadro's number, $6.022\,140\,857 \times 10^{23} = N_A$ of that something.

Avogadro's number not only bridges the microscopic and the macroscopic, but it also allows us to make mass conversions. Now, you may ask, how does it allow for us to find the mass, if it only has to do with the number of something that we are dealing with? It turns out that Avogadro's number is specifically chosen for that purpose. Remember when we said that Avogadro's number is the number of atoms in 12 grams of carbon-12? The 12 is the nucleon number of carbon. Nucleon numbers are usually denoted by the capital letter A. This means that when we add the number of protons to the number of neutrons, we get 12.

As you can see, Avogadro's number is huge. A mole of pennies ($6.022\,140\,857 \times 10^{23}$ pennies) is enough to give everyone on the earth about 850 billion dollars! The constant is named in honor of Amedeo Avogadro, and it is the number of carbon-12 atoms in 12 grams of a pure sample of carbon-12. Carbon-12 is a specific isotope of carbon. Isotopes of an element have the

same chemical properties, but different masses. Thus, it is important to state the specific isotope in this case. Using this constant, we can make conversions. I will do analogous calculations with a dozen of eggs as well, to draw parallels between the two.

$$1 \text{ dozen eggs} = 1 \text{ dozen x eggs}$$

$$1 \text{mol pennies} = 1 \text{ mole x pennies}$$

Note that mole is written as mol, in shorthand notation.

Then, we use the appropriate conversion factors. It is important to note that these conversion factors are all equal to 1.

We have:

$$12 \text{ of something} = 1 \text{ dozen of something}$$

Therefore, we have the following conversion factor:

$$\frac{12 \text{ of something}}{1 \text{ dozen of something}} = 1$$

Likewise, we have:

$$6.022\,140\,857 \times 10^{23} \text{ of something} = 1 \text{ mole of something}$$

Therefore, we have the following conversion factor:

$$\frac{6.022\,140\,857 \times 10^{23} \text{ of something}}{1 \text{ mole of something}} = 1$$

Dividing out the "of something" and the 1, we can rewrite the conversion factors as follows. Note that they have inverse units.

$$12 \text{x} \frac{1}{\text{dozen}}$$

$$\text{Avogadro's number} = N_A = 6.022\,140\,857 \times 10^{23} \text{x} \frac{1}{\text{mol}}$$

Thus, we can now complete the conversion as follows:

Chapter 2: Conservation

$$(1 \text{ dozen x eggs}) \left(12\text{x} \frac{1}{\text{dozen}}\right) = 12 \text{ eggs}$$

$$(1 \text{ mol x pennies})(N_A) = (1 \text{ mol x pennies}) \left(6.022\ 140\ 857 \times 10^{23}\text{x}\frac{1}{\text{mol}}\right)$$

$$= 6.022\ 140\ 857 \times 10^{23} \text{ pennies}$$

We see that, not only do we arrive at an equivalent value, because we simply multiplied by a fraction that is equal to one, but the units of something is kept. When converting, we absolutely do not convert seconds into meters! Thus, we obtain a value that is physically the same as the previous, but only measured using a different scale.

Origins of Stoichiometry

In any given situation, matter is conserved. Matter consists of mass and energy. In short, the famous equation $E = mc^2$ says that mass and energy are the same thing. They are both ways to measure amounts of matter. Conservation may be applied to calculate the results of chemical reactions, because when we sum the mass and energy before a reaction, we should get the same value as if we sum the mass and energy after the reaction. The calculation of the relative amounts of reactants and products for a given reaction is called stoichiometry, which is the measurement (metron) of the elements (stoicheion) in Greek.

Basic Results of Conservation, and the Laws of Constant Proportions and Composition

Stoichiometry is based upon the idea of conservation, and it also leads to many important principles. In 1794, Joseph Proust published his law of constant proportions after studying iron oxides. Proust's law of constant proportions means that for any amount of a pure compound, the ratio between the types of atoms that make up the compound is a constant. For example, in a pure sample of Iron(III) Oxide, Fe_2O_3, the ratio between iron atoms and oxygen atoms will always be 2:3, because the ratio of Fe^{3+} ions to O^{2-} ions need to be balanced in order to make a neutral compound. It also meant that the ratio of the mass of iron to the mass of the compound would be the same. If you generalize the law of constant proportions, you get an equivalent

Chapter 2: Conservation

statement, which is the law of constant composition. Both laws ensure that the elements that make up a pure sample of a compound is always the same, and in the same relative amounts. Therefore, carbon dioxide will always have 2 oxygen atoms for each carbon atom, otherwise the molecule is not carbon dioxide.
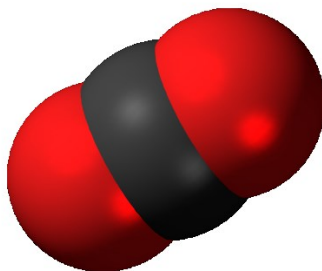
Figure 2.1. A space-filling model of carbon dioxide, showing that the molecule is composed of two oxygens (red) and one carbon (gray).

Likewise, a molecule of water is always H_2O, consisting of two hydrogens and one oxygen put together.
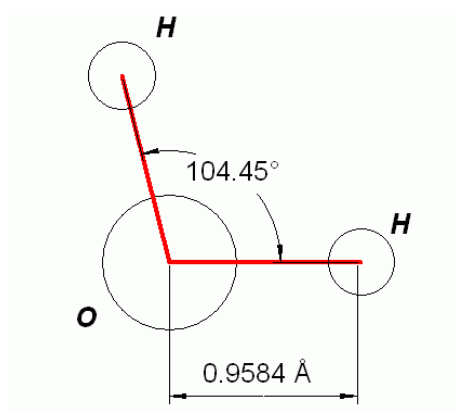
Figure 2.2. A detailed ball and stick model of water, showing that the molecule is made of two hydrogen atoms connected to one oxygen atom.

Atomic Theory

Proust's law was not readily accepted, because most scientists at the time did not agree with the existence of atoms. They believed that proportions of atoms are nonsensical because there are no atoms. In the fifth century BCE, Democritus of Abdera already suggested that there

Chapter 2: Conservation

may be distinct particles of matter, which he named "atomos" for indivisible. However, because Aristotle and Plato opposed Democritus's theory of matter, the concept of the atom was lost in time, and was not widely accepted in 1794. It was not until John Dalton proposed the atomic atom again in 1803 did the atom become a common concept. Dalton's early atomic theory is still held to be valid today. The only postulate which is marginally wrong is that atoms cannot be divided, created, nor destroyed. Although atoms do not undergo those changes in chemical reactions, nuclear reactions can divide, destroy, and create atoms. Even then, matter is conserved, because the sum of the final mass and energy is equal to the sum of the initial mass and energy.

Dalton's Atomic Theory

Dalton proposed the following in his atomic theory:

1. Atoms are very small particles that make up elements

2. Atoms of an element are identical, but atoms of different elements are different.

3. Atoms are the smallest unit of elements that retain the properties of the element, and can participate in chemical reactions.

4. Atoms are not changed in chemical reactions. They are not divided, created, nor destroyed. Chemical reactions simply reorganize the atoms that participate in the reaction.

5. Compounds are products of reactions, and they have a fixed ratio between the atoms that make up the pure compound. (Proust's law of constant proportions and constant composition). Molecules and ionic substances are all compounds.

Chemical Equations

Most of the time, when we write a chemical reaction, it should be balanced. That means that there are the same number of atoms of each element on the left side as there are on the right side. Not only does this conserve atoms, it also conserves mass. It makes sense that if the number of atoms of each element is the same on both sides, then both sides should have the same mass. Balanced equations are useful. Although unbalanced reactions are not equations at all, sometimes

Chapter 2: Conservation

they are called unbalanced equations. They are not equations, because what is on the left side does not equal what is on the right side. Unbalanced reactions are not very useful until they are balanced, because they tell us the reactants and products of the reaction, but not the ratios of reactants that are necessary, nor the amounts of products that are produced.

Unbalanced reaction:

$$H_2 + O_2 \rightarrow H_2O$$
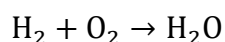
Looking at both sides, we note that there is an extra oxygen on the left side. This means that this is not an equation, because the two sides are not equivalent. We cannot use this to see how much water is made from a set amount of hydrogen molecules. However, we can balance it by guessing, and we get the balanced equation:

$$2H_2 + O_2 \rightarrow 2H_2O$$
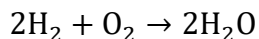
Note that when balancing, we can only change the coefficients, but not the subscripts. Changing the coefficients changes the number of each reactant and product involved, but changing the subscripts changes the identity of the substances. Thus, note that all species are still the same, but some are just multiplied. We can use the balanced equation to convert between reactants and products. Note that there are the same number of each type of atom on both sides. Thus, if we want 10 water molecules, we need 10(2) atoms of hydrogen, because water is $2 * H + 1 * O$. Therefore, we need 20 atoms of hydrogen, which is equal to 10 molecules of hydrogen.

$$10(2) \text{atoms of hydrogen} = 20H = 10 * 2H = 10H_2 = 10 \text{ } H_2 \text{ molecules}$$

Standard States of Matter

Matter is said to be at standard conditions, if it is at Standard Ambient Temperature and Pressure (SATP), which is 298.15 Kelvins, and 1 atmosphere. Usually, SATP is indicated by the degree symbol, °. Most data sources are tabulated at SATP. SATP is approximately the temperature and pressure conditions in your room right now. To convert that to familiar units, we have the following:

Chapter 2: Conservation

For temperature:

$$T \text{ in Kelvins} = T \text{ in Celsius} + 273.15$$

$$T \text{ in Celsius} = (T \text{ in Farenheit} - 32) \text{x} \frac{5}{9}$$

For pressure:

$$1 \text{ atm} = 1.01325 \text{ bars} = 1.01325 * 10^5 \text{ pascals}$$

When we do the conversion, we find it to be at about 25 degrees Celsius, which is equal to 77 degrees Fahrenheit. Since the atmosphere is determined by measuring the pressure at sea level, and most land is above sea level, the pressure in your room is probably slightly less than the pressure at sea level. This is because the atmospheric pressure is related to how much air is above the location. If you are higher up, there simply is less air above you, thus the atmospheric pressure would be lower. The reason why we chose these conditions to be our standard conditions is because most reactions will be carried out in environments close to these conditions. Every reaction that we conduct in open air is at a constant pressure of about 1 atmosphere, and most reactions in a regular room occur at about 298.15 K. However, do note that there is also Standard Temperature and Pressure (STP), represented by a superscripted plimsoll symbol, $\ominus$, which is at 273.15 K and 1 bar of pressure. The two are not interchangeable. However, sometimes it is convenient to work with STP, especially for thermodynamics, because the bar is equal to 10^5 pascals, and the pascal is the SI derived unit for pressure, whereas the pressure in atmospheres must be first converted.

Example Reaction: The Haber-Bosch Process

Conservation allows us to predict the products of a certain reaction, or find what is necessary for a reaction to occur. For example, in the famous Haber-Bosch process, we produce ammonia, NH_3, from N_2 and H_2 gas. The following balanced thermochemical reaction will be used to demonstrate stoichiometry.

Haber-Bosch process:

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) + 92.4 \frac{kJ}{mol}, T \approx 670 \text{ K} - 720 \text{ K}, \text{Fe Cat.}, p \approx 25{,}500 \text{ kPa}$$

Chapter 2: Conservation
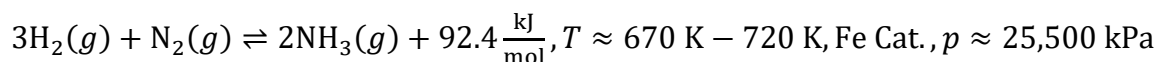
States of Matter, and Reaction Conditions

Each reactant and product is called a species. The letter in the parentheses that follow the species indicate the physical state of the species. Here, the H_2, N_2, and the NH_3 all are gases. We also write (*aq*) for aqueous solutions in water, (*s*) for solid, and (*l*) for liquid. The two harpoons indicate a state of equilibrium, which means that the reaction can go both ways depending on the conditions. Here, the conditions are forcing (high temperatures, and high pressures), because we need to make the reaction proceed to the right to generate useful product. If we did not specify temperature, we can simply use the $\xrightarrow{\Delta}$ symbol to indicate that the reaction needs to be heated to proceed.

Balance of Atoms, and Application of Proust's Law

We were provided with the balanced equation for the Haber Bosch process. A balanced equation means that the reactants have the same amount of matter as the products, and that the atoms in the products are the same ones as the atoms in the reactants. We see that for each ammonia molecule, we need a nitrogen atom and three hydrogen atoms. Thus, every time an ammonia product molecule is formed, we consume a nitrogen and three hydrogen reactant atoms. When we make two ammonia atoms, we consume 3 molecules of gaseous hydrogen, and one molecule of gaseous nitrogen. The ratio of nitrogen to hydrogen is one to three on both sides of the equation.
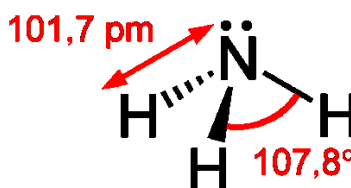
Figure 2.3. An ammonia molecule is composed of three hydrogen atoms bonded to a nitrogen atom.

Chapter 2: Conservation

Energy Balance and Enthalpy

The energy of the reaction is on the products side. This means that the reaction released energy, which is lost to the environment. In chemistry, the convention is to always look from the perspective of the atoms and molecules, because chemistry is the study of the atoms and molecules. Since the atoms and molecules are what is important, we define our system to be the atoms and molecules. Systems are collections of objects, and they contain matter. In our reaction above, the initial atoms to the left lost the energy to the environment when the reaction takes place to form the molecules to the right. Thus, we say that the change in enthalpy of the reaction at constant pressure is $\Delta H = -92.4$ kJ/mol. ΔH is the symbol for the change in enthalpy of the reaction, which is equal to the heat released by the reaction if the reaction takes place in a situation with constant pressure.

Constant pressure may be found in a reaction vessel, as in the example above, or more commonly, when a reaction is conducted in open air. The value is negative, because when heat is released by the reaction, our system, the atoms which become molecules, lost energy to the environment. If our reaction gains energy from the environment, then the enthalpy of reaction would be positive. Likewise, we would write the energy on the reactants side of the balanced equation. When a reaction releases energy, the environment heats up. For example, when we burn wood, the reaction releases energy, so you feel the warmth, the thermal energy. We say that these reactions are exothermic. When a reaction consumes energy, the environment cools down because the environment must supply the energy to the reaction that requires energy, and very often the energy is from thermal energy. Therefore, when you melt ice, you feel the coldness as energy is used to melt the ice. We say that these reactions are endothermic.

Figure 2.4. The dissolution of ammonium nitrate in water is an endothermic reaction used in instant ice packs (left). The rapid oxidation of aluminum is an exothermic reaction, as seen in the thermite reaction (right).

Note that the units of the enthalpy of reaction is in kilojoules per mole. We measure the enthalpy of reaction as the heat released by a mole of that reaction taking place at constant pressure, because the reaction of a very few molecules does not generate anything measurable. However, when we multiply that by Avogadro's number, we get a measurable quantity, and that measurable quantity is quite big, often being on the magnitude of thousands of joules. We write the enthalpy as per mole, because for every mole of that reaction taking place, we have a set amount of energy that will be transferred. If, for example, we reverse the reaction. Then, we simply negate the change in enthalpy, and we write the corresponding reaction by switching the products to the reactants side, and the reactants to the products side.

$$2NH_3(g) + 92.4\frac{kJ}{mol} \rightleftharpoons 3H_2(g) + N_2(g), T \approx 670\ K - 720\ K, \text{Fe Cat.}, p \approx 25{,}500\ kPa$$

$$\Delta H = 92.4\frac{kJ}{mol}$$

Chapter 2: Conservation
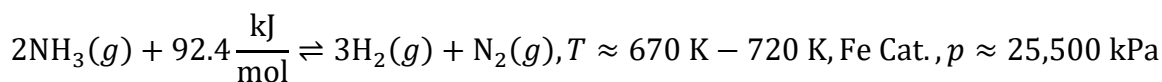
Theoretical Yield

Calculation by Moles

Let's say that we need 1,000 moles of ammonia, because the Haber-Bosch process is usually run on an industrial scale. In the balanced equation, the number preceding a reactant or a product is called a stoichiometric coefficient. We see from the balanced equation that the ratio of the stoichiometric coefficients of $N_2(g)$ to that of $NH_3(g)$ is 1:2, and the ratio of the stoichiometric coefficients of $H_2(g)$ to $NH_3(g)$ is 3/2:1, or equivalently, 3:2. This means that one mole of N_2 gas is stoichiometrically equivalent to 2 moles of ammonia, and 3 moles of H_2 gas is stoichiometrically equivalent to 2 moles of ammonia gas. We write it as follows: $1N_2 \simeq 2NH_3$, and $3H_2 \simeq 2NH_3$. Also, 1 mole of N_2 is stoichiometrically equivalent to 3 moles of H_2, so $1N_2 \simeq 3H_2$. This means that we need 1 mole of nitrogen gas to make 2 moles of ammonia, and we need 3 moles of hydrogen gas to make 2 moles of ammonia. It also means that for every mole of nitrogen gas consumed in the reaction, 3 moles of hydrogen gas are also consumed, and vice versa. Therefore, to make 1000 moles of ammonia, we would need 500 moles of nitrogen gas (1000 moles of nitrogen atoms), and 1500 moles of hydrogen gas (3000 moles of hydrogen atoms). The amount of energy that the reaction would release is $500 \text{ mol}_{rxn} \times 92.4 \frac{kJ}{mol_{rxn}} = 46200$ kJ, because we need 500 moles of the balanced reaction above to get 1000 moles of NH_3. However, it is also common to write the balanced equation as follows, and any multiple of the balanced equation is acceptable.

$$\frac{3}{2}H_2(g) + \frac{1}{2}N_2(g) \rightleftharpoons NH_3(g) + 46.2\frac{kJ}{mol}, T \approx 670\text{ K} - 720\text{ K}, \text{Fe Cat.}, p \approx 25{,}500\text{ kPa}$$
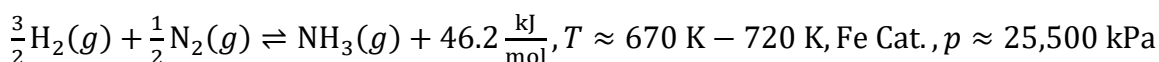
Thus, we find that making a mole of ammonia releases 46.2 kJ of heat, and $46.2\frac{kJ}{mol_{rxn}} \times 1000\text{ mol}_{rxn}$ is also equal to 46200 kJ. We can perform the calculation, as long as the thermochemical equation is balanced.

Calculation by Mass

If, instead of moles, we want the mass of the products and reactants, we can refer to the periodic table. The periodic table usually has two numbers for an element, and one is the atomic mass of an element, and the other is the atomic number. The mass number is recorded in grams

Chapter 2: Conservation

per mole, because a single atom has a relatively insignificant mass. This mass is also the mass of a single atom in Daltons, which is a unified atomic mass unit equal to 1 gram per Avogadro's number. Thus, an Avogadro's number of the atom's mass would give the mass in grams of a mole of that atom, which is equal to the mass number. We call the mass per mole of molecules, atoms, and compounds the molar mass, M.

The atomic mass is always equal to or greater than the atomic number, and usually is around double the atomic number. The reason I say equal to is because in the special case of protium, the most common type of hydrogen with no neutrons, the atomic mass is fairly equal to the atomic number, 1. However, for most other elements, a good rule of thumb is that atomic mass is about two times the atomic number. The mass numbers are not whole numbers because some elements exist as different isotopes which have different numbers of neutrons in the nucleus, thus leading to differences in mass. However, for a given element, the atomic number is always equal because all isotopes of an element have the same number of protons and electrons. When we tabulate the atomic masses, we do a weighted average of the isotopes, so that we have an accurate representation of the average mass of the element found on earth. Chlorine is a popular example.

Mass Numbers of The Periodic Table, and The Example of Chlorine

Chlorine has 2 main isotopes. The others are present in such small amounts that they are insignificant, and are called trace isotopes. One isotope is chlorine-35 (Natural abundance=75.77%, 17 protons, 18 neutrons), and the other is chlorine-37 (Natural abundance=24.23%, 17 protons, 20 neutrons). Natural abundance is the percent of atoms of an element that exist as the specific isotope.

To calculate average atomic mass, we do the following:

1. Convert all the abundance percentages to fractions. The easiest way is to just divide by 100.
    a. 0.7577/1 of all the chlorine on earth is chlorine-35, and 0.2423/1 of the chlorine on earth is chlorine-37

Chapter 2: Conservation

2. Multiply their atomic mass, in atomic mass units, by the fraction that we obtained previously. This allows for us to perform an average of all of the isotopes based upon their importance by abundance. Then, we add them together.

a. $0.7577(35) + 0.2423(37) = 35.4$ grams per mole.

This process gives a value close to what we observe for a sample of the element on earth. You can also find the natural abundance of the isotopes if you are given the average atomic mass, and the masses of the isotopes. Thus, the average mass of a chlorine atoms is 35.4 grams per mole. However, in nature, chlorine exists as diatomic chlorine molecules, Cl_2, and a mole of chlorine gas molecules has a mass of 35.4 grams/mol x 2 moles= 70.8 grams.

By Moles and by Mass

Thus, if we want 1000 moles of ammonia, we would want:

$1000(\text{molar mass of ammonia}) = 1000\big(1(\text{molar mass of N}) + 3(\text{molar mass of H})\big) =$

$1000\text{moles}(14.01 + 3\text{x}1.008)\text{grams/mole} = 17034$ grams of Ammonia

Which would require $1000(\text{molar mass of N}) = (1000)(14.01) = 500(\text{molar mass of N}_2) =$

$500(14.01 * 2) = 500(28.02) = 14010$ grams of Nitrogen

and $3000(\text{molar mass of H}) = 3000(1.008) = 1500(\text{molar mass of H}_2) = 1500(2.016) =$

3024 grams of Hydrogen

Note that 14010 g +3024 g = 17034 g! The mass of the reactants should always be approximately equal to the mass of the products, because matter is conserved. However, in any reaction, the mass of the reactants is never truly equal to the mass of the products, because change in energy needs to also be accounted for. In an exothermic reaction, where the heat leaves the system, the mass decreases by a tiny amount. The exact opposite happens in an endothermic reaction. This difference in mass is pretty much insignificant in normal chemical calculations, but is absolutely necessary to conserve matter, as mass and energy are both forms of matter. However, in nuclear reactions, there is a significant change in mass, because of the very large

Chapter 2: Conservation

amounts of energy involved. The change in mass due to the transfer of energy is described by Einstein's iconic $E=mc^2$.

Likewise, we can do this in reverse. The number of moles of hydrogen gas needed for 17034 grams of ammonia is 1500. Note how Proust's law of constant proportions and the law of constant composition is held. No matter how much ammonia is present, in a pure sample of ammonia the mass ratio of the nitrogen in the sample to the mass of the sample is always 14.01 to 16.016, and the number of nitrogen atoms is always a third of the number of hydrogen atoms present. Likewise, the same holds for hydrogen. Thus, conservation of matter allows us to perform calculations of energy and matter, thus allowing us to write balanced thermochemical equations to describe reactions.

Experimental Yield Calculations, and Efficiency

Calculating Reactant Amounts

However, certain reactions don't finish. In fact, the large majority of reactions do not go to completion, and instead, reach an equilibrium state where the reaction cannot proceed anymore. Thus, there is a theoretical yield, and an experimental yield. Theoretical yield is the quantity of products that can be produced if the reaction goes to completion. Experimental yield is how much we get when we carry out the reaction in real life. Dividing the experimental yield by the theoretical yield provides a metric of the reaction's efficiency in converting reactants to products. This may be expressed in a percentage. For example, in the Haber-Bosch process, the yield is approximately 15%, before the reaction cannot proceed anymore. Thus, we only get about 15% of the maximum amount of ammonia that can be made with all the molecules. However, chemical engineers have found a way around that, and we will revisit the process when we talk about equilibrium. To find how much reactants we actually need, we do the theoretical yield calculation to find the theoretical amounts of reactants, and then we divide the theoretical amounts of reactants by the experimental-theoretical yield ratio.

$$\text{How much reactant is needed} = \frac{\text{theoretical reactant amount}}{\left(\frac{\text{experimental yield}}{\text{theoretical yield}}\right)}$$

Chapter 2: Conservation

Limiting Reactants

Also, in some reactions, there is not enough reactant to drive the reaction to completion. This is a case of a limiting reactant. The limiting reactant is the first reactant to run out. To find out which reactant is the limiting reactant we use the balanced equation, and do a series of theoretical yield calculations. With information provided on how much reactants there is, along with the balanced equation, we can calculate how much of the product can be formed with each reaction, and how much of the other reactants are necessary. For example, when sodium is put in water, it generates hydrogen gas and enough heat to ignite the hydrogen gas violently. The balanced equation is below:

$$2\text{Na}(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{NaOH}(aq) + \text{H}_2(g), \Delta_{rxn}H^{\ominus} = -368.4 \text{ kJ/mol}$$
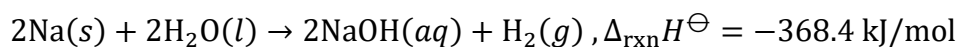
Note that there is the Plimsoll symbol superscript above the enthalpy symbol. That means that the reaction takes place under Standard Temperature and Pressure (STP) conditions, at a temperature of T=273.15 K and a pressure of 1 Bar (100 kPa). Also, we like to indicate the process that is occurring by putting a subscript under the delta before the enthalpy symbol. This means that the change in standard enthalpy of the reaction is -368.4 kJ/mol. That is a negative number with a very large magnitude, and reflects the large amount of energy released by the reaction.

Example of the Reaction of Sodium Metal and Water

If in this given case we are provided 1000 g of H_2O, and 1100 g of Na metal, and we proceed with the dangerous reaction that may kill us, the reaction will not completely consume all the reactants. In this case, one of the reactants is a limiting reactant. So, from the balanced equation, we observe that $2\text{Na} \simeq 2\text{H}_2\text{O} \simeq 2\text{NaOH} \simeq 1\text{H}_2$, or equivalently, $1\text{Na} \simeq 1\text{H}_2\text{O} \simeq 1\text{NaOH} \simeq 1/2\text{H}_2$. Whichever way you prefer it does not matter. You can just write the stoichiometric coefficients with all the products and reactants in a line for a balanced equation, and then just say they are stoichiometrically equivalent. Now, knowing the relation between the reactants in moles, we must do a series of theoretical yield calculations. This reaction was chosen because it essentially goes to 100% completion, which means that you will run out of the limiting reactant. For an inefficient reaction, you may not run out of reactants because the reactants cease reacting. However, here you may assume that the reaction is driven

Chapter 2: Conservation

until one of the reactants is exhausted. So, we divide the mass of each reactant by its molar mass to obtain the number of moles of each reactant. Then, we use the stoichiometric ratios to determine how much product can we make. The reactant which leads to less product being possibly made is the limiting reactant, as that will run out first, and stop the reaction from proceeding further because there is nothing left to react. The calculation is shown as below:

For H_2O:

$$\frac{1000g\ H_2O}{(16.00 + 1.008x2)\frac{g\ H_2O}{1\ mol\ H_2O}} = 55.5062\ moles\ of\ H_2O$$

$$\frac{55.062\ mol\ H_2O}{\frac{2\ mol\ H_2O}{2\ mol\ NaOH}} = 55.062\ moles\ of\ NaOH$$

For Na:

$$\frac{1100g\ Na}{22.99\frac{g\ Na}{mol\ Na}} = 47.8469\ moles\ of\ Na$$

$$\frac{47.8469\ mol\ Na}{\frac{2\ mol\ Na}{2\ mol\ NaOH}} = 47.8469\ moles\ of\ NaOH$$

By this point, by calculating with one product, we already know that Na is the limiting reactant, because the amount of Na that we have can produce less product than the amount of H_2O that we have. However, if we check with the other product, we obtain the same conclusion. To find how much product is produced, find the smallest theoretical yield, the theoretical yield of the limiting reactant, and that is the amount of product that will be formed. From a single product, we can then convert to the other products, since we have the balanced equation, and know the stoichiometric calculations. Also, from knowing the limiting reactant, we know how many moles of the balanced reaction took place. Thus, from that information, we can also calculate the change in enthalpy of this reaction. For this reaction, $\Delta_{rxn}H^{\ominus} =$

$-368.4\frac{kJ}{mol_{rxn}}$x23.9234 mol_{rxn} $= -8813.4$ kJ. 23.9234 moles of the balanced reaction took

Chapter 2: Conservation

place, because the number of moles of NaOH produced is twice the number of moles of reaction that took place, because of the stoichiometric coefficient of 2 in front of the NaOH in the balanced thermochemical equation. Most stoichiometry-related stuff are just a series of boring calculations. However, it is necessary to understand stoichiometry to understand deeper topics.

Approximations

Approximations are commonly applied when writing thermochemical equations. For example, the following two ways of writing a thermochemical reaction are balanced, because the same amount of matter are on the left and right of the arrow.

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g) + 368.4 \text{ kJ}$$

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g), \Delta_{rxn}H^{\ominus} = -368.4 \text{ kJ/mol}$$
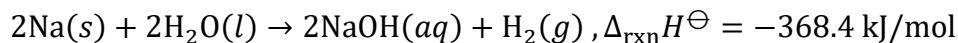
However, very often, we also see the same reaction represented as follows:

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$
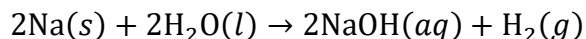
Whoever wrote that approximated the energy to be an insignificant amount of matter. Although the equation is technically incorrect, it is a shorter way to represent the reaction. Note that the amount of matter on the left is not the same as the amount of matter on the right, because the right is missing the 368.4 kJ of energy. However, if we mass both sides, we will see very little difference, because the amount of matter neglected in the equation is equal to 4.1×10^{-12} kg. Therefore, the approximation is still very close, close enough that the difference is not physically significant. Because it is so close, we will write most equations in the approximate form to save space and time. In chemical reactions, the energy does not need to be considered in the mass balance. Likewise, the mass should not be considered in the energy balance. The two are separated by several magnitudes of scale because of the mass-energy relation, and that allows us to simplify, approximate, and separate the calculations. However, always keep in the back of your mind that the energy does matter! In nuclear reactions, there is a far larger difference in energy, which leads to significant differences in mass, and the energy cannot be neglected.

Chapter 2: Conservation

Ions

Energy and mass are conserved because of the conservation of matter. This leads to another important result, which is the conservation of charge. Charge is locally conserved because the particles that carry charge are conserved in chemical reactions. We do not consume protons and electrons when reactions occur. Therefore, if we sum up all of the charges of the non-neutral species on one side, we should get the same result if we sum up all the charges of the non-neutral species on the other side. For example, consider the following reaction:

$$2AgNO_3(aq) + CaCl_2(aq) \rightarrow 2AgCl(s) + Ca(NO_3)_2(aq)$$
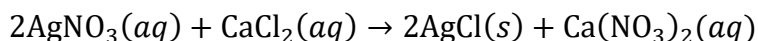
Note that if I sum up all the charges on the left side, I get the same result as if I sum up all the charges on the right side.

$$2(0) + (0) = 0 = 2(0) + (0)$$

Since the two ionic compounds on the reactant side are in aqueous solution, they disassociate into their corresponding ions. Thus, we can also write the equation as follows:

$$2Ag^+(aq) + 2NO_3^-(aq) + Ca^{2+}(aq) + 2Cl^-(aq) \rightarrow 2AgCl(s) + Ca^{2+}(aq) + 2NO_3^-$$
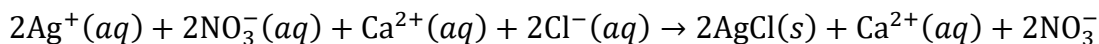
The same applies here.

$$2(+1) + 2(-1) + (+2) + 2(-1) = 0 = 2(0) + (+2) + 2(-1)$$

Thus, we see that since chemical reactions do not destroy atoms and subatomic particles, charge is conserved. If you check, in any balanced reaction, the number of protons and electrons are the same on both sides.

Net Ionic Equation

To simplify calculations, we sometimes write a net ionic equation for reactions in solution. A net ionic equation only includes species relevant to the reaction. Ions that do not participate in the reaction are called spectator ions. When writing net ionic equations, we only include products that are produced by the reaction, reactants that are consumed to form the products, insoluble compounds, weak acids, and weak bases. For example, in the following reaction, only ions that directly react are included. The sodium cation and the nitrate anion are

spectator ions. This is a common classroom demonstration of a precipitation reaction. The AgCl is said to be precipitated out of solution when the Ag^+ ion forms an insoluble complex with the Cl^- ion.

Reaction with all ions included:

$$Ag^+(aq) + NO_3^-(aq) + Na^+(aq) + Cl^-(aq) \rightarrow AgCl(s) + NO_3^-(aq) + Na^+(aq)$$
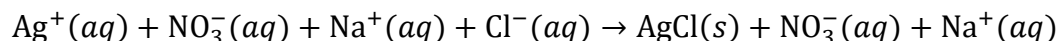
Net ionic equation:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$
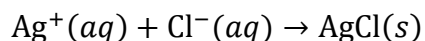
Also, in the following example, we show that weak acids and bases are always included, because they do not completely disassociate.

$$CH_3COOH(aq) + OH^-(aq) \rightarrow H_2O(l) + CH_3COO^-(aq)$$
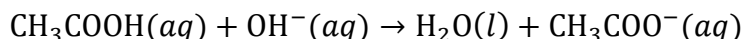
In the above cases, charge is conserved. This result is important, if we are given a reaction that is not balanced. By balancing the atoms and charge on both sides, we can find the balanced equation.

Balancing Equations

Very often, we are given reactions that are not balanced. For example, if we are given the following:

$$AgNO_3(aq) + CaCl_2(aq) \rightarrow AgCl(s) + Ca(NO_3)_2(aq)$$
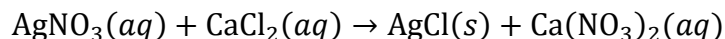
You have already seen this reaction, and if you don't remember, you can just guess to balance the reaction as follows:

$$2AgNO_3(aq) + CaCl_2(aq) \rightarrow 2AgCl(s) + Ca(NO_3)_2(aq)$$
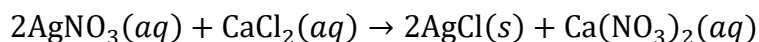
However, it will not always be this simple. There are three common methods to balance chemical equations. The first, is to guess. Guessing usually will work for simple reactions. To guess, we begin with the species containing the element that occurs the least amount of times. Then, we try numbers until we get our solution. This is a very unscientific method to balance reactions, but is faster for some problems. The second method is to make a system of equations

Chapter 2: Conservation

that involves all the atoms on both sides. The third method is to set up a system of equations to balance mass and charge. We do not commonly set up equations with energy, because energy is very difficult to measure in some circumstances, and we do not have very good standards in how to exactly determine the energy of certain systems and species under various conditions. Those techniques may be found in most basic chemistry textbooks, and will not be necessary for our purposes here.

Chapter 3: Particles and Ideal Gases

The Kinetic Molecular Theory

Since many theories on energy are developed from the behavior of gases, we will discuss gases first. According to the Kinetic Molecular Theory of Matter (KMT), matter is composed of numerous particles that are constantly in motion. The KMT is applied to systems where there are enough particles for the average overall behavior of the system to be measurable. Usually, there are far more than enough particles in systems that we normally interact with (for example, anything you see has way more atoms than you can count). For these systems, we can define properties such as volume, temperature, pressure. When measuring the given property, we can do so with a certainty that we have a value that is pretty much constant at a given moment. Because the random motion of the particles creates these measurable properties, we say that the system is stochastic. Stochastic systems depend on the sum of the random actions of the particles. If we have enough particles to make the system stochastic, as in most samples of gases, we arrive at the same constant value when we add up the actions of the individual particles. The Kinetic Molecular Theory of Matter explains to us that the gas is simply just a collection of loosely related particles in random motion. However, to simplify calculations, we approximate. This is done by assuming that the substance we are dealing with is an ideal perfect gas (which does not exist).
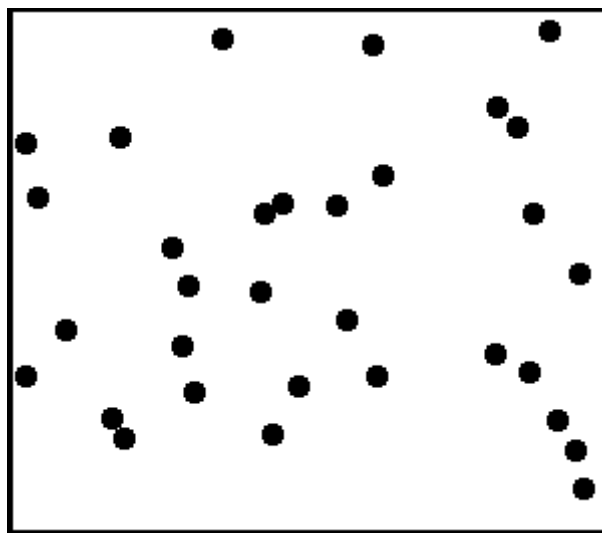
Figure 3.1. A collection of randomly moving gas particles.

The Ideal Gas

The ideal gas is a very important concept, and is frequently used in calculations. The ideal gas follows the Kinetic Molecular Theory of Matter along with a few additional postulates. Together, these form the Kinetic Molecular Theory for Ideal Gases. The ideal gas has properties as follows:

Property from Kinetic Molecular Theory of Matter:
1. Gases are made of numerous particles that are in random motion in space.

Additional Properties that an Ideal Gas Has:
1. Gas molecules have no volume. Therefore, they are point masses, and have all their mass concentrated at the center.
2. Gas molecules do not have any interactions besides collisions.
3. Gas molecules do not lose any energy in collisions with each other or the walls of the system. Thus, all collisions are perfectly elastic.
4. The energies of gas molecules depend on the temperature, and only the temperature. This means that the gas molecules only have kinetic energy, because heat is kinetic energy on the microscopic scale.

These properties are important, as they simplify our calculations on the behavior of gases so that we can make general observations concerning all gases. Real gases have many deviations from the assumptions listed above. For example, real gases do not have all the mass concentrated at a single point. However, the size of an atom is approximately an angstrom, which makes the mass distribution of the gas molecule very close to the center of the molecule. Also, real gases do transfer energy when they collide, and real gases do have potential energy. Therefore, although the ideal gas is theoretically useful, assuming ideal gas behavior when designing a reactor will probably lead to explosions. However, there are gases that exhibit ideal-like behavior. For example, noble gases are monatomic and almost perfectly spherical. They also do not have any significant interactions. Therefore, noble gases behave similarly to the ideal gas, with helium being the most ideal of all real gases.

Chapter 3: Particles and Ideal Gases

Properties of Ideal Gases, and the Ideal Gas Law

Boyle's Law of Pressure and Volume

To define an ideal gas, we must first consider some properties of real gases. The first two gas properties that were found to be related are pressure and volume. Robert Boyle, an early experimenter in the field, published his law in 1662. Boyle's law of pressure and volume states that pressure and volume are inversely proportional. Thus, they are related by a constant of inverse proportionality. Boyle's law can be written as the following, where p is the pressure, and V is the volume of the gas:

$$p \propto \frac{1}{V} \quad \text{therefore } pV = c, \text{where } c, \text{temperature, and amount of gas are constants}$$
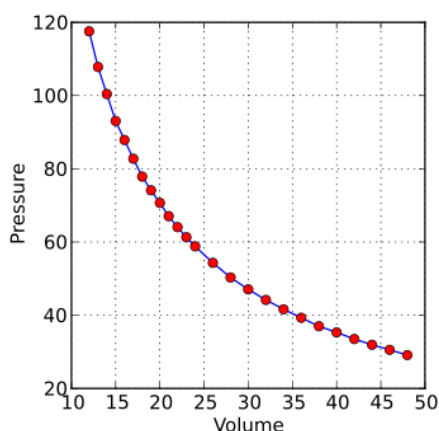
Figure 3.2. A graph of pressure versus volume, with temperature kept constant. The graph shows that pressure decreases when volume increases, and volume decreases as pressure increases, as predicted by Boyle's law. This type of curve is expected for inverse relations.

From the same law, we can write many equivalent statements:

$$p_1 V_1 = p_2 V_2 \qquad \frac{p_1}{V_2} = \frac{p_2}{V_1} \qquad \frac{p_1}{p_2} = \frac{V_2}{V_1}$$

This means that doubling the pressure halves the volume, doubling the volume halves the pressure, and vice versa. Note the conditions that are stated at the side. Holding temperature and amount of gas constant is very important, as changing these variables affects the pressure and the volume. Note the subscripts 1 and 2. These indicate states. A state is a defined condition of the system where all the properties of the system are strictly defined. For example, when the system

Chapter 3: Particles and Ideal Gases

with 1 moles of nitrogen gas is at T=298.15 K and 1 atm pressure (SATP), and a volume of 24.789 liters. We will find out later that to specify all the variables in a system that consists of an ideal gas, we only need to specify 3 variables.

      Robert Boyle, and his student, Robert Hooke, discovered the law by putting a set amount of gas in a manometer, and then adding mercury.
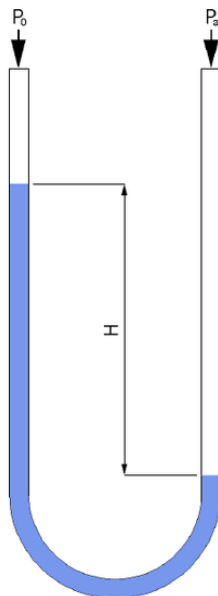
Figure 3.3. A diagram of a manometer. The pressure is measured by recording the height difference between the two arms, which is equal to the difference of pressures p_0 and p_a in millimeters of the fluid. Thus, if the fluid is H_2O, then the pressure could be expressed in mmH$_2$O, or if the fluid is in mercury, the pressure could be expressed in mmHg. Thus, the measured pressure, p_a, can be found by using the equation $\boldsymbol{p_a = Hg\rho + p_0}$, where ρ is the density of the fluid, H is the height difference, g is the acceleration due to gravity, which is approximately equal to $\boldsymbol{g \approx 9.81\frac{m}{s^2}}$ at the surface of the earth, and p_0 is the reference pressure. If the reference pressure is equal to zero, then the equation simplifies to $\boldsymbol{p_a = hg\rho}$. The density of water is approximately 1 gram per cubic centimeter, and the density of mercury is approximately 13.56 grams per cubic centimeter. Thus, we find that 1 atm is equal to 760 torr, or 760 mmHg (named after Torricelli, the inventor of the barometer), which is equal to 10332 mmH$_2$O.

They found that when they doubled the pressure by increasing the amount of mercury, the volume of the gas roughly halved, and vice versa. Boyle was one of the first experimental chemists, and he set up a rudimentary laboratory that allowed him to be one of the first pioneers that applied the scientific method rigorously.

Chapter 3: Particles and Ideal Gases

Charles' Law of Volume and Temperature

The second gas law relates temperature and volume. Jacques Charles discovered the law in the 1780's. Charles' law, written mathematically, is as follows, where V is the volume and T is the temperature of the gas:

$$V \propto T \text{ therefore } \frac{V}{T} = c, \text{ where } c, \text{ pressure, and amount of gas are constants.}$$
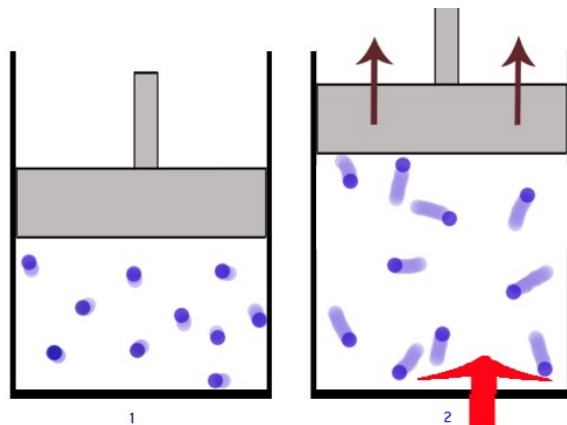
Figure 3.4. The higher the temperature, the faster and more frequently the molecules strike the walls of the container. Therefore, if the piston is free to move, and if the container is kept at constant atmospheric pressure, the gas will expand.
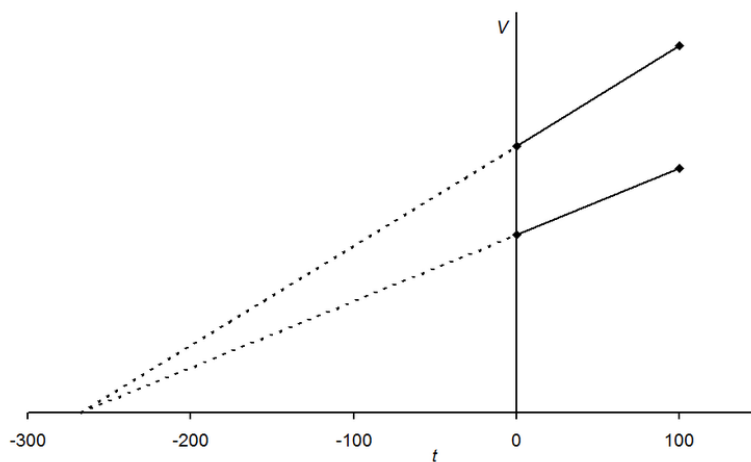
Figure 3.5. A graph of volume versus temperature for two experiments. Note how both lines extrapolate to a point where the volume is theoretically zero, and the temperature is -273.15 degrees Celsius, or absolute zero (0 K).

Chapter 3: Particles and Ideal Gases

Note, that when the graph of volume versus temperature is extrapolated, we get zero volume when the temperature is equal to 0 K, or -273.15 degrees Celsius. This allows for us to estimate absolute zero, and all gases should ideally converge to absolute zero when extrapolated, as shown for the two gases in the graph above.

Jacques Charles had a hobby of making early flight machines, and discovered the law when making hot air balloons. Like Boyle's law, Charles' law of volume and temperature can also be rearranged into many equivalent statements:

$$V_1 T_2 = V_2 T_1 \qquad \frac{V_1}{T_1} = \frac{V_2}{T_2} \qquad \frac{V_2}{V_1} = \frac{T_2}{T_1}$$

This means that doubling the volume halves the temperature, and doubling the temperature doubles the volume, and many other equivalent statements.

Amontons' Law of Pressure and Temperature

Two laws are classically attributed to Gay-Lussac. However, the law relating temperature and pressure is now usually attributed to Guillaume Amontons, as Amontons discovered the law in 1699, whereas Gay-Lussac made his discovery between 1800 and 1802. Amontons' law of pressure and temperature is commonly also called Gay-Lussac's gas law of pressure and temperature. It is written as follows, where p is the pressure and T is the temperature of the gas:

$$p \propto T \text{ therefore } \frac{p}{T} = c, \text{ where } c, \text{volume, and amount of gas are constants}$$

Gay-Lussac was making gas thermometers, and in the process, discovered the law. However, Amontons, who was working with J-tube thermometers a hundred years earlier already discovered the law by using boiling and cold water. The law can also be written as follows:

$$p_1 T_2 = p_2 T_1 \qquad \frac{p_1}{T_1} = \frac{p_2}{T_2} \qquad \frac{p_1}{p_2} = \frac{T_1}{T_2}$$

Likewise, we give a similar interpretation as the previous two laws, that doubling pressure doubles temperature, doubling temperature doubles pressure, and vice versa, with all other variables held constant. In 1702, Amontons found with his law that the temperature needs to be negative 240° Celsius below the freezing point of water for the volume of a gas to be zero. Thus,

Chapter 3: Particles and Ideal Gases

he was the discoverer of absolute zero. He was 33.15 degrees off, and we now know absolute zero to be at -273.15 °C, or 0 K. Amontons did not use Celsius, as that temperature scale was not invented until 1742 by Anders Celsius, but rather used his own measurement system based off his thermometer.

Gay Lussac's Law of Combining Volumes

Gay-Lussac's law of combining volumes, found in 1808, states that when we have all gaseous products and reactants, the number of moles of gas before and after the reaction are proportional to the number of moles of gas that are on the product side and reactant side of the balanced thermochemical equation if the products are at the same temperature and pressure as the reactants. He found the relation by burning 2 portions hydrogen and 1 portion oxygen forms 2 portions of water.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) + \ 484 \text{ kJ}$$
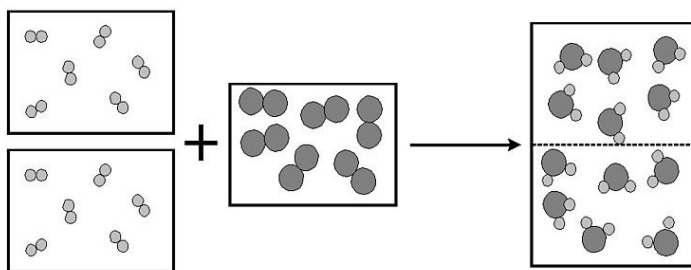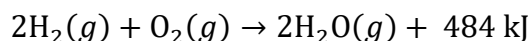
Figure 3.6. Reacting 2 volumes of hydrogen and 1 volume of oxygen, will form 2 volumes of water.

Thus, burning 2 liters of hydrogen and 1 liter of oxygen forms 2 liters of water vapor. This also implies that the number of moles of gas present at a given pressure and temperature is proportional to the volume of the gas. When combined with Proust's law, this leads to yet another gas law, which is Avogadro's law of volumes and moles.

Chapter 3: Particles and Ideal Gases

Avogadro's Law of Volumes and Moles

Avogadro's gas law of volumes and moles states that the amount of gas present is proportional to the volume of the gas at a given temperature and pressure. This can be expressed as the following, where V is the volume and n is the number of moles of the gas:

$$V \propto n \text{ therefore } \frac{V}{n} = c, \text{where c, p, T are held constant}$$

The constant of proportionality, c, varies with temperature and pressure. However, the volume of a mole of gas at two common states are good to know. The molar volume of an ideal gas at Standard Temperature and Pressure (STP, T=273.15 K, p=1 bar) is 22.414 liters, and the molar volume of an ideal gas at Standard Ambient Temperature and Pressure (SATP, T=298.15, p=1 atm) is 24.789 liters. Amedeo Avogadro proposed his law as a hypothesis in 1811. However, it was not accepted until 1860, when it was successfully presented to the First International Congress by Stanislao Cannizzaro.

Dalton's Law of Partial Pressures

Following the Kinetic Molecular Theory of Gases, we also find another significant result. When we have a mixture of ideal gases, the total pressure of the mixture is equal to the sum of the individual pressures of the individual ideal gas components, which are proportional to the composition of the mixture. This is known as Dalton's law of partial pressures. It was discovered by John Dalton in 1801. That means that a mixture of one mole of gas A and two moles of gas B has a pressure of $p_A + p_B = p_{total}$, and that the pressure of gas B will be twice the pressure of gas A, because the concentration of gas B is twice that of gas A. Thus, $p_B = 2p_A$, and $p_{total} = 3p_A = 3p_B/2$.

Chapter 3: Particles and Ideal Gases
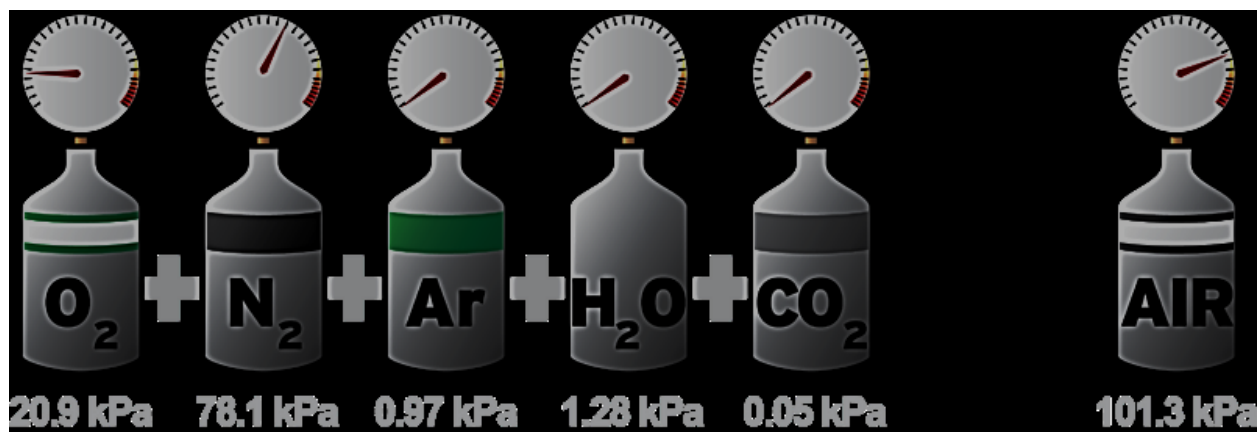
Figure 3.7. Adding all of the partial pressures of all of the gases in the atmosphere yields a total pressure of 1 atm, which is equal to 101.3 kPa.
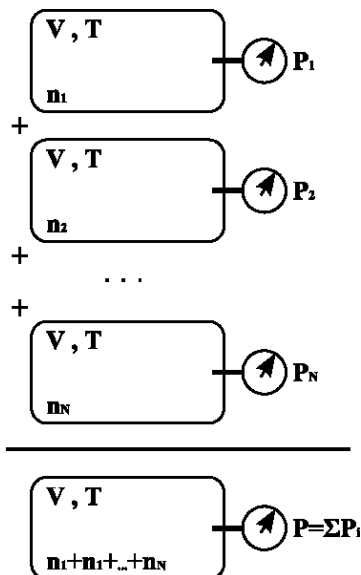
Figure 3.8. Putting all the gases in the above containers into a single container causes the single container to have a pressure that is equal to the sum of the pressures of the above containers.

The concentration of components in a gaseous mixture may be specified as percentage of gaseous molecules, molarity, or more commonly, what is known as a mole fraction. Mole fractions are calculated by dividing the number of moles of that specific gas, by the total number of moles in the container. Thus, mole fractions for gases A, B, C, …, represented as $x_A, x_B, x_C, ...$, all add up to one for a given mixture:

Chapter 3: Particles and Ideal Gases

$$x_A = \frac{n_A}{n_{mixture}} = \frac{\text{\# molecules of gas A}}{\text{\# molecules of mixture}} = \frac{\text{\# of moles of gas A}}{\text{\# of moles of gas in the container}}$$

$$x_A + x_B + x_C + \cdots = 1$$

Therefore, given the previous relation, we have:

$$p_A + p_B + p_C + \cdots = p_{total}$$

Amagat's Law of Partial Volumes

Since pressure and volume are related by Boyle's law, we also arrive at Amagat's law of partial volumes, which states that the sum of the volumes of each individual component is equal to the total volume of the mixture.

$$V_A + V_B + V_C + \cdots = V_{total}$$
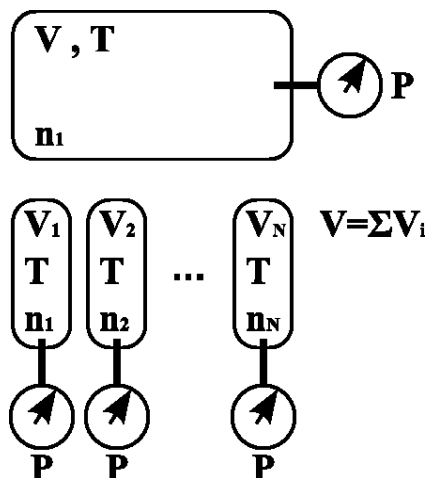
Figure 3.9. At constant pressure, the volume of a mixture of gases is equal to the sum of the volumes of the individual gases that make up the mixture.

Émile Amagat published his law of partial volumes in 1880, and it can be deduced from laws previously introduced.

It is self-explanatory that you can find the total amount of gas molecules in a container by adding the number of moles of each type of gas.

Chapter 3: Particles and Ideal Gases

$$n_A + n_B + n_C + \cdots = n_{\text{total}}$$

Conditions for the Aforementioned Gas Laws to Hold

For these principles to hold, we need the components of the ideal gas mixture to be at the same temperature. Since the ideal gases are mixed, usually we can assume that the temperature of the mixture is the same throughout, and apply these principles. Also, they do not hold for non-ideal gases, because they are based upon the assumption that the ideal gas mixture is composed of ideal gases.

The Combined Gas Law

Émile Clapeyron put Boyle's and Charles' laws together in 1834. This is known as the combined gas law. When we put together all the gas laws, we find that:

$$\frac{pV}{T} = b, \text{ where b is a constant if the amount of gas is constant}$$

This can also be written as:

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

By holding a variable constant, we can find the change in one variable that is caused by changing another variable. Here, it does not matter what units pressure and volume are expressed in, as all pressure and volume scales are proportional to each other. However, note that the same does not apply to temperature, as the temperature scales are not proportional to each other. The temperature needs to be in Kelvins.

I named the constant b, because there is something special about this constant. Experimentally, we find that b is equal to the number of gas particles present, multiplied by the Boltzmann constant, k. The Boltzmann constant, k, is equal to $1.380\,648 \times 10^{-23}$ J K^{-1}. It relates the absolute temperature of a gas with the average kinetic energy of the gas particles. If we have two moles of gas, then b is equal to 2 moles $* N_A * k$, where N_A is Avogadro's number. Thus, we take two moles of particles and multiply them by the Boltzmann constant to find b.

Chapter 3: Particles and Ideal Gases

However, very often, it is far more convenient to set the unit of amount to moles, rather than number of individual particles. Thus, we arrive at the molar gas constant, which is equal to the Avogadro's number times the Boltzmann constant.

$$N_A k = 8.314\ 472\ \text{J K}^{-1}\text{mol}^{-1} = 8.314\ 472\text{x}10^{-2}\ \text{L bar K}^{-1}\text{mol}^{-1}$$

The constant is given in different units. However, for our case, because we are using liters, bars, kelvins and moles as our units of volume, pressure, temperature, and amount, we will use the second value given, which is $R = 8.314\ 472\text{x}10^{-2}\ \text{L bar K}^{-1}\text{mol}^{-1}$. However, later when we talk energy, we will use the first one, as our energy unit, the joule, is conveniently included. However, if you do some dimensional analysis with the units, you will find that you can convert the first into the second, and vice versa. They are equivalent. Now, we can express our special constant, b, as nR. R is the molar gas constant for liters, bar, kelvin and moles. The lowercase n is used to symbolize the number of particles, in moles. Now if we want to find the constant b for 2 moles of gas, we simply do $2R$. Much easier!

The Ideal Gas Law

However, here is where it hits the fan for the constant. That b is NOT a constant! In fact, it is the constant R, multiplied by the number of moles in the system, n! Thus, rearranging, we get a very special law, the ideal gas law. This law perfectly describes all ideal perfect gases.

$$\frac{pV}{T} = nR \rightarrow pV = nRT$$

This is a very important result, as it will be used in numerous derivations to follow! The ideal gas law is an equation of state, as it describes the set of conditions a given gas is in. A distinct set of conditions is called the state of a system, and we change the state as we change the conditions.

Limitations of the Ideal Gas Law

Although the previous gas laws are useful in thermodynamic proof-writing and for approximating gaseous behavior, real gases frequently deviate from the idealizations of the Kinetic Molecular Theory of Gases. For example, real gases do have volume, attractive and

Chapter 3: Particles and Ideal Gases

repulsive interactions, and potential energy. The energies of the gas particles are also not completely kinetic, because as mentioned, the particles do have potential energy. The mass of the particles is not concentrated at the center, especially for polyatomic gases. They break every property of the ideal gas, to some extent or another. However, there are situations where real gases approximate ideal behavior, such as in the case of low pressure, where the gas molecules are far apart from each other and do not have significant interactions, or when temperature is high, where the high kinetic energies of the gas molecules make all other energetic interactions insignificant.

Effusion

Effusion is the escape of gas from a container through a small hole. Although on a large scale we usually attribute the escape of gas to pressure, pressure is the result of collision of the gas particles with the wall of the container on a microscopic scale. Thus, it is often a bit of confusion on what causes the gas to leave the container. Pressure does not drive the gas to leave. In fact, there is nothing that drives the gas to leave. Imagine a container full of molecules that are in constant random motion. The number of molecules that strike the wall of the container is roughly the same at any instant. Thus, the pressure is just a measure of how hard the molecules hit the wall of the container. The more molecules there are, the more molecules collide with the walls at a given instant. Likewise, the higher the temperature, the faster the molecules move, again leading to more frequent collision, and in this case, collisions with more momentum. Thus, increasing the number of molecules in the container, or temperature of the preexisting molecules, leads to an increase in pressure.

Effusion is Due to Random Motion and Newton's First Law

Now, imagine that there is a piece of the wall of the container that is missing. Therefore, all of the molecules that were going to collide with that piece of the wall now leave the container, and keep on moving in accordance with Newton's first law, that objects in motion remain in constant motion if not acted upon by a net force. That is effusion.

Chapter 3: Particles and Ideal Gases
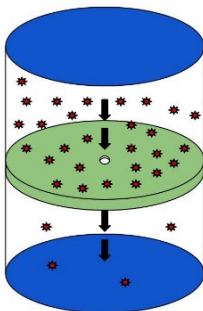
Figure 3.10. Effusion occurs when gas particles that are already in random motion escape through a small hole.

Diffusion is just effusion on a larger scale. Thus, the random motion of all of the particles is what causes the particles to leave the container. From this, we can reason that the rate at which the particles leave is proportional to the mean velocity of the particles.

$$\text{Rate} = sv \text{ where } v \text{ is the mean velocity of the collection of particles,}$$
$$\text{and s is some constant of proportionality.}$$

$$\text{Rate} \propto v, \text{where } \propto \text{ means proportional to.}$$

Thus, dividing two rates and two velocities, we have:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{(\text{mean velocity})_1}{(\text{mean velocity})_2} = \frac{v_1}{v_2}$$

Graham's Law of Effusion: Relating Kinetic Energy to Rate of Escape

Thus, we use the equation for kinetic energy to relate the mean velocity and the mass of the particles, in order to arrive at a relation between the mass and rate of effusion.

$$\text{Kinetic energy} = K = \frac{1}{2}mv^2, \text{where } m \text{ is in kilograms, and } v \text{ is in } \frac{m}{s}$$

$$\sqrt{\frac{2K}{m}} = v$$

Chapter 3: Particles and Ideal Gases

Here, it is seen that the mean velocity is inversely proportional to the square root of the mass of the particles. Dividing the mean velocities for particles of two different mean energies, we arrive at our first expression of Graham's law of effusion.

$$\frac{v_1}{v_2} = \frac{\sqrt{\frac{2K_1}{m_1}}}{\sqrt{\frac{2K_2}{m_2}}} = \sqrt{\frac{\left(\frac{K_1}{m_1}\right)}{\left(\frac{K_2}{m_2}\right)}} = \sqrt{\frac{K_1 m_2}{K_2 m_1}} = \frac{\text{Rate}_1}{\text{Rate}_2}$$

From this, we see that the rate of effusion is inversely proportional to the square root of the masses of the two gases. Thus, if we have two gases at the same kinetic energy, then the rate of effusion would be slower for the gas with a higher molar mass.

$$\frac{\text{Rate}_1}{\text{Rate}_2} \propto \sqrt{\frac{m_2}{m_1}}$$

For ideal gases, which follow the KMT for ideal gases, the kinetic energy is proportional to the square root of temperature. Thus, at the same temperature, an ideal gas that is four times as massive will effuse two times slower, or at half the rate. From this, we can find a relation between rate and temperature for ideal gases. Because we also observe that rate is proportional to kinetic energy, we have the following relation that only holds true for ideal gases, but is a fairly good approximation for gases at low pressure and high temperature:

$$K = sT \text{ for ideal gases, where s is some constant of proportionality}$$

$$\text{For ideal gas,} \frac{\text{Rate}_1}{\text{Rate}_2} \propto \sqrt{\frac{T_1}{T_2}}$$

So, putting all of the equations together, we have the following relations:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{v_1}{v_2} = \frac{\sqrt{\frac{2K_1}{m_1}}}{\sqrt{\frac{2K_2}{m_2}}} = \sqrt{\frac{\left(\frac{K_1}{m_1}\right)}{\left(\frac{K_2}{m_2}\right)}} = \sqrt{\frac{K_1 m_2}{K_2 m_1}} \propto \sqrt{\frac{m_2}{m_1}} \propto \sqrt{\frac{K_1}{K_2}}$$

And, for an ideal gas, the previous all hold true, with one additional relation:

Chapter 3: Particles and Ideal Gases

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{v_1}{v_2} \propto \sqrt{\frac{K_1}{K_2}} \propto \sqrt{\frac{T_1}{T_2}}$$

Concentration, Molar Mass, and Density of an Ideal Gas

Concentration

Other quantities and relations that may be useful from the ideal gas equation are gas concentration and density. For any gas equation, the concentration is simply the inverse of the molar volume.

$$\text{Molar volume} = V_\text{m} = \frac{V_\text{gas}}{1 \text{ mol of gas}}$$

$$\text{Concentration in molarity} = \text{M} = \frac{\text{moles of gas}}{\text{liter of space}} = \frac{1}{V_\text{m}} = \frac{1 \text{ mol of gas}}{\text{molar volume}}$$

For an ideal gas, $\text{M} = \frac{n}{v} = \frac{p}{RT}$

Density and Molar Mass

For any gas equation, the density is always equal to the molar mass of the gas multiplied by the concentration, which is equal to the molar mass of the gas multiplied by the number of moles of gas per unit volume, or the inverse of the molar volume. Do not confuse the non-italicized M above, which means molarity, with the italicized M below, which means molar mass:

$$\text{Density} = \rho = \frac{\text{mass of gas}}{\text{volume of gas}} = \frac{(\text{molar mass of gas})(\text{moles of gas})}{\text{Volume of gas}}$$

$$= \frac{(\text{mass per mole of gas})(\text{moles of gas})}{\text{Volume of gas}} = \frac{M}{V_\text{m}}$$

Therefore, for an ideal gas, $\frac{M}{V_\text{m}} = \frac{Mp}{RT}$, and from $pV = nRT \rightarrow \frac{n}{V}(M) = \rho \rightarrow \frac{pM}{RT} = \rho$

For an ideal gas, it is very easy to find the density once the molar mass of a gas is known, and it is also very easy to find the molar mass of the gas if the density is known.

Chapter 3: Particles and Ideal Gases

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws

Limiting Laws, and Approaching Ideal Gas Behavior

Before you read this section, it is highly recommended that you read the limits portion of the introduction to calculus. This is because the concept of a limit is helpful and necessary to understand the ideas presented below. Ideal gases are based upon the concept of the limit, because real gases become ideal under extreme, limiting conditions.

Boyle's Law Holds for Real Gases When Pressure Approaches Zero

One situation is when the pressure of the gas approaches zero. Likewise, for this to happen with all other variables held constant, volume must approach infinity. Boyle's law of pressure and volume holds perfectly when pressure approaches zero, and volume approaches infinity. Thus, we write:

$$pV = c \text{ when } \lim_{p \to 0} \text{ or } \lim_{V \to \infty}$$

Boyle's law is an example of a limiting law. A limiting law only holds when a variable approaches some limit. In this case, when pressure approaches zero, or volume approaches infinity. The limit just means that the variable stated under the limit approaches some value, which is the number to the right of the arrow. Boyle's law holds at the limit when p approaches zero, because that is when the concentration of particles is low. Therefore, the particles rarely collide, and do not repel nor attract one another. Thus, there are no longer any interactions. The space separating the particles becomes infinitely large as the pressure of the gas becomes infinitely small. The same argument is when the volume is made very large.

The gas is more ideal for the same reasons, and when the pressure is infinitely low, volume needs to be infinitely large according to Boyle's law. On the other hand, when the pressure is large, and the volume is small, the particles are close to one another and interact frequently. There is a substantial amount of repulsive and attractive interactions, as the particles are not separated by a large amount of space. Thus, not all the energy of the particles is kinetic. Some of it is potential energy. Also, perfectly elastic collisions do not exist in nature. You will never see a dropped ball bounce back to the same height. Likewise, as the particles collide, they

do transfer energy with the environment, thus more collisions lead to more instances where gas molecules violate the constant kinetic energy principle of the Kinetic Molecular Theory of the Ideal Gas. Because the gas particles are not point masses, when volume of the gas becomes low, pressure shoots up because of a sharp increase in repulsive interactions. Thus, the amount of pressure needed to create a corresponding decrease in volume is much higher than the pressure calculated by Boyle's law. When this happens, eventually the gas will likely condense into a liquid. During condensation, the pressure is at a constant maximum. When all the gas has condensed, the pressure shoots up sharply, because it is far more energetically unfavorable to compress a liquid than a gas due to the strong repulsions that take place.

Charles' Law Holds for Real Gases When Temperature Approaches Infinity

Another limiting law is Charles' law. Charles law holds when the temperature is high, and, with all other variables held constant, when volume is large:

$$\frac{V}{T} = c \text{ when } \lim_{V \to \infty} \text{ or } \lim_{T \to \infty}$$

Note that temperature should approach infinity if volume approaches infinity at constant pressure. We already explained why infinite volume leads to more ideal behavior. High temperatures also lead to more ideal behavior, because when the temperature increases, the higher velocity of the particles mean that the energies of the interactions between the particles become insignificant. The more temperature, the more percentage of the total energy of the particles is due to kinetic energy. However, if temperature is low, then the interactions between the particles become significant, and the ideal gas assumptions fall apart. When temperature becomes very low, real gases tend to condense into a liquid, and their behavior completely deviates from that of an ideal gas.

Amontons' Law Holds for Real Gases When Temperature Approaches Infinity or When Pressure Approaches Zero.

Amontons' law is also limiting, in that:

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws

$$\frac{p}{T} = c \text{ when } \lim_{p \to 0} \text{ or } \lim_{T \to \infty}$$

We already explained why the limits make the law approach ideal gas behavior.

Relating the Gas Laws

Notice how each of the limiting gas laws above contain a pair of variables. Also, note that with all other variables held constant, the two variables in each relation approach the limits stated simultaneously. This is not a coincidence, as the variables are all related to one another through the ideal gas law. Since the independent relations that make up the ideal gas law is limiting, the ideal gas law is a limiting law. The ideal gas law is an equation that embodies the Kinetic Molecular Theory for an Ideal Gas. Therefore, it holds when the behavior of the gas is ideal. Thus, the ideal gas law holds when the pressure is small, volume is large, and the temperature is high. Although some of these conditions can occur when the number of moles of gas is decreased, I do not state that here. It is very important to the theory that the number of gas molecules is large enough to be stochastic. Therefore, although decreasing the number of gas molecules decreases gas density if volume is held constant, it does not hold in a limiting case, when the number of gas molecules is zero. No gas, no gas law. The ideal gas law obviously does not hold when applied to a vacuum.

The Compression Factor

A method of measuring how close a gas is to being ideal is by using the compression factor. The compression factor is found by dividing the volume of the gas by the volume of an ideal gas under the same conditions. Thus, it is expressed as follows:

$$Z = \frac{V_{\text{real gas}}}{V_{\text{ideal gas}}} = \frac{V_{m,\text{real gas}}}{V_{m,\text{ideal gas}}}$$

Note that we can use molar, because the units cancel. In fact, we can use any unit of amount of gas. For an ideal gas, $Z=1$. Also, in the limiting cases where real gases resemble ideal gases, the compression factor is approximately 1. Any deviation from 1 is an indicator of deviation from ideal gas behavior. If $Z<1$, then attractive forces are significant, and the gas occupies less volume

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws

than predicted by the ideal gas equation. This usually is observed when the molecules are close enough that they attract each other, but not close enough for strong repulsive forces to become significant. If $Z>1$, then repulsive forces are significant, and the volume is greater than that predicted by the ideal gas equation. This occurs when the gas molecules are very close to one another, which is when the conditions are the opposite of the ideal limiting conditions. Thus, it is an indicator that provides us a feel of how ideal a gas behaves in a given set of conditions.

Molar Quantities

The ideal gas law can be plotted as a surface, and various sections of that surface yields graphs that represent each of the gas laws. For example, take a surface of one mole of gas. It is convenient to express p, V, and T when the number of moles of gas, n, is one. That way, we can perform the physically meaningful calculation, and then scale it up to the size of the system. Thus, we define molar quantities, such as the molar volume, V_m, at STP and at SATP, and other temperatures and pressures and conditions. Also, this conveniently leaves us a graph of three variables, which we can plot as a three-dimensional surface, which is easy to see. In a graph of p versus V_m, with temperature held constant, we get a hyperbolic curve. This is an isotherm, or a graph where temperature is held constant. In the hyperbola, we obviously see the characteristic graph of an inverse relation. However, if we graph p versus $1/V_m$, we get a straight line because pressure is directly proportional to the inverse of molar volume. If we plot the constant pressure isobars for the V versus T graph, we see a straight line, because volume and temperature are directly related. Likewise, if we plot the constant volume isochores for the p versus T graph, we get a straight line, as pressure and temperature are directly related.

Derivation of the van der Waals Equation of State

Since the ideal gas equation is not perfect, there have been numerous attempts to find equations that describe real gases more accurately. They each have their strengths and shortcomings. However, a historically notable equation of state is the van der Waals equation of state, formulated by Johannes Diderik van der Waals in 1873. This is another approximation, although it works better than the ideal gas equation, because it accounts for some attractions with

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws

a factor a, and repulsions due to the volumes of the particles, with a factor b. The two factors compensate for increase in gas volume because of the volume of the gas molecules themselves, and for decreases in gas pressure because of attractive interactions.

Derivation of the van der Waals Equation

The derivation begins with the ideal gas law:

$$pV = nRT$$

It is easier to use the ideal gas law in molar form for most derivations:

$$pV_m = RT$$

We add a factor to the pressure, so that the calculated pressure is lower when all other variables are kept constant:

$$(p + x)V_m = RT$$

Here, if temperature, number of moles, and molar volume are kept the same, the calculated p is x less than the p calculated by the ideal gas law, because p is now replaced by $(p+x)$.

$$p_{\text{calculated with ideal gas equation}} = \frac{RT}{V_m} > p_{\text{calculated with van der waals equation}} = \frac{RT}{V_m} - x$$

Likewise, to increase the calculated volume, we subtract a factor from the volume:

$$p(V_m - y) = RT$$

This has a similar effect, where the calculated volume is now y greater than the volume calculated by the ideal gas law, if p, n, and T are kept constant.:

$$V_{m,\text{calculated with ideal gas equation}} = \frac{RT}{p} < V_{m,\text{calculated with van der waals equation}} = \frac{RT}{p} + y$$

Putting these two together, we get an equation of the following form:

$$(p + x)(V_m - y) = RT$$

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws

Here, x is a square parameter, and y is a linear parameter:
  Since pressure is due to collisions of gas particles with the walls of the container, and attractive interactions both decrease the velocity and frequency of the collisions, x is a square parameter, because it affects the pressure in two ways. So, we substitute in d for x:

$$(p + (d)^2)(V_\text{m} - y) = RT$$

Since volume of the particles only adds to the total volume of the gas, y is a linear parameter. So, we have an equation of the same form as above. Then, we need some further derivations to obtain d and y.

$$(p + (d)^2)(V_\text{m} - y) = RT$$

Pressure reduction:
  The pressure is reduced by the square of some constant multiplied by the inverse of the molar volume. This makes sense, because pressure is roughly inversely related to molar volume, as shown by Boyle's law. Thus, increasing the molar volume allows the pressure to decrease, if temperature is held constant.

We Substitute the Inverse of the Molar Volume for Concentration:
  Molar volume is equal to the inverse of gas concentration.

$$V_\text{m} = \frac{V_\text{gas}}{1 \text{ mol gas}}$$

$V_\text{m} = \dfrac{1}{M}$, where M is gas concentration in molarity $\left(\dfrac{\text{moles}}{\text{liter}}\right)$. Therefore, $M = \dfrac{1}{V_\text{m}}$

Different molar volumes mean different gas concentrations. Concentration affects attractive and repulsive interactions that alter the pressure. Now, substituting $(d)^2$ for $\left(k\dfrac{1}{V_\text{m}}\right)^2$, where k is some constant, we have:

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws

$$\left(p + \left(k\frac{1}{V_\text{m}}\right)^2\right)(V_\text{m} - y) = RT$$

Perfect Hard Sphere Assumption:

For the next part of the derivation, we consider the gas molecules to be perfect hard spheres. The hard sphere assumption is valid for most gases. If necessary, we can change that assumption, and arrive at similar results. If we consider the minimum distance between the centers of two hard spheres, we find it is equal to $2r$. Thus, because of the presence of a gas particle, the center of another gas particle cannot be inside a sphere with a radius of $2r$ that is concentric with the center of a gas particle. Therefore, since the volume of a hard sphere is equal to $V = \frac{4}{3}\pi r^3$, the volume in space that the center of another gas molecule cannot be in is equal to $V = \frac{4}{3}\pi(2r)^3$. Thus, the volume that the center of the gas molecule cannot be in is equal to $V = 8 * \frac{4}{3}\pi r^3$, or 8 times the volume of a single atom. Since the interaction is between two gas molecules, we divide the volume excluded by two, to get an approximate average of how much volume each gas molecule excludes. Thus, each gas molecule excludes an average volume of approximately $V_\text{excluded} \approx 4 * \frac{4}{3}\pi r^3 = 4 * V_\text{single molecule}$, or four times the volume of a hard sphere gas molecule. Because we are working with the molar form of the equation, the y is approximately equal to Avogadro's number multiplied by the average excluded volume.

$$y \approx N_A * V_\text{excluded} \approx N_A * 4V_\text{single molecule}$$

Through this entire process, we assumed that the molecules are either monatomic, or behave with a high degree of symmetry. We can approximate excluded volumes of other molecules, if we change that fundamental assumption, and make a similar calculation as shown above. However, since the excluded volume is most commonly experimentally determined anyways, let's continue with our derivation:

Arriving at the van der Waals Equation of State

We define a new constant, a, which is equal to k^2:

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws

$$\left(p + a\left(\frac{1}{V_{\text{m}}}\right)^2\right)(V_{\text{m}} - y) = RT, \text{where } a = k^2$$

And another new constant, b, which is equal to y:

$$\left(p + a\left(\frac{1}{V_{\text{m}}}\right)^2\right)(V_{\text{m}} - b) = RT, \text{where } b = y$$

Now, all we need to do is some rearranging to arrive at our result, the molar form of the van der Waals equation of state!

$$p + \frac{a}{V_{\text{m}}^2} = \frac{RT}{(V_{\text{m}} - b)}$$

$$p = \frac{RT}{(V_{\text{m}} - b)} - \frac{a}{V_{\text{m}}^2}$$

Converting Between Molar and Non-molar forms

To get the non-molar form, we simply multiply the numerator and denominator of the term that includes V_{m} to the first power by n, and multiply the numerator and denominator of the term that includes V_{m} to the second power by n^2. Multiplying the numerator and denominator by the same non-zero value is the same as multiplying by 1. Therefore, we do not disturb the equality of the equation. We multiply by powers of n because $V_{\text{m}} = V/n$, which means that $V_{\text{m}} * n = V$.

$$p = \frac{nRT}{n(V_{\text{m}} - b)} - \frac{n^2 a}{n^2(V_{\text{m}}^2)}$$

$$p = \frac{nRT}{(nV_{\text{m}} - nb)} - \frac{n^2 a}{(n^2 V_{\text{m}}^2)}$$

$$p = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2}$$

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws

Van der Waals Equation of State

$$p = \frac{nRT}{V - nb} - a\left(\frac{n^2}{V^2}\right), \text{and in molar form}, p = \frac{RT}{(V_\mathrm{m} - b)} - \frac{a}{V_\mathrm{m}^2}$$

The van der Waals Constants

The constants a and b are called van der Waals constants. They are experimentally determined for each gas, and the equation only holds empirically. The equation is very important, as increasing the volume decreases the term that includes the factor a, and increasing the volume makes the nb insignificant. At infinite volume, the term including the a can be approximated to zero, and *V-nb* can be approximated to *V*. Rearranging, we arrive at *pV=nRT*, the ideal gas equation. Thus, a gas described by the van der Waals equation becomes more ideal when volume increases. Also, when temperature increases, the *a* term becomes insignificant, and this also makes the behavior of the gas more ideal. Pressure is related to the other two, and for a given amount of gas, can be found using the temperature and volume of the gas if the constants a and b are known.

Critical Constants of a van der Waals Gas

Although for the most part the surface resembles that of the ideal gas law, there are a few important deviations. A plot of volume, pressure, and temperature of the van der Waals equation provides an interesting result. When the temperature exceeds a certain value, there are these nonsensical loops. For example, along certain isotherms, volume decreases with increasing pressure. That is physically impossible. Therefore, we again approximate, and we draw horizontal lines that cut these loops with equal area above and below the line. These lines are called Maxwell constructs, after James Clerk Maxwell, who did further investigation into the work of van der Waals.

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws
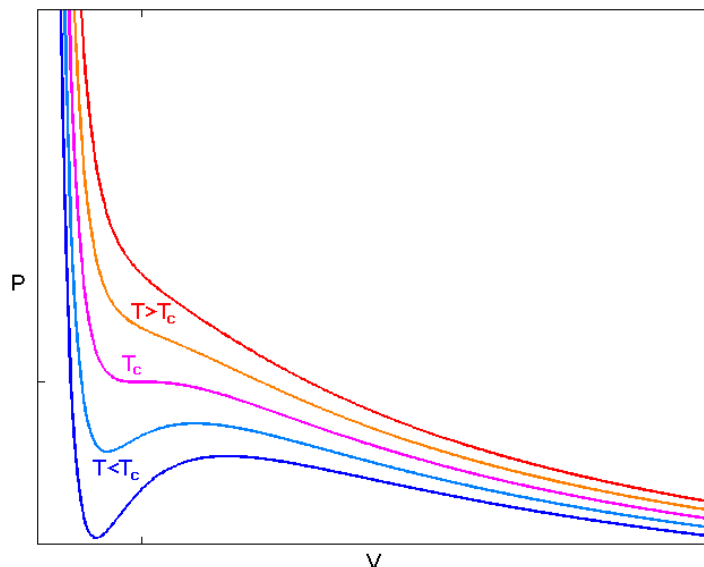
Figure 4.1. Isotherms (*p* versus *V* graphs at constant temperature) of a van der Waals gas. When the temperature is above the critical temperature, we get an impossible result, where the pressure decreases with decreasing volume. Thus, we bridge the loops by drawing horizontal lines called Maxwell constructs.

The Critical Temperature

The temperature stated previously is not just an arbitrary temperature. It is a very special temperature, called the critical temperature. It is the temperature above which the gas cannot be liquefied by increasing the pressure of the gas. Above this temperature, further compression forms a supercritical fluid, in which the pressure continues to increase, and the fluid becomes increasingly dense. In a supercritical fluid, the surface, or interface, between liquid and gas is not well defined, and does not exist. Below the temperature, there is a clear surface that separates liquid from gas during liquefication, and pressure during compression at a fixed temperature below the critical point reaches a constant maximum during condensation. After all the gas becomes a liquid, the pressure required for further compression sharply shoots up. At this critical temperature, there is a critical point, which has a set value for pressure and volume. We can describe three properties at the critical point, called critical properties. They are the critical temperature, T_c, critical molar volume, $V_{m,c}$, and the critical pressure, p_c. The critical properties of each gas are different, and are experimentally obtained.

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws

Solving for the Critical Constants:

      The critical constants for a van der Waals gas are derived by solving differential equations obtained by setting the first derivative of the pressure with respect to the molar volume equal to zero, and the second derivative of the pressure with respect to the molar volume equal to zero. Notice how, even though the correct way to write the second derivative of pressure with respect to molar volume, which applies the differential operator $\frac{d}{V_m}$ twice, is technically:

$$\left(\frac{d}{dV_m}\right)\left(\frac{d}{dV_m}\right)(p) = \left(\frac{d}{dV_m}\right)^2 (p) = \frac{d^2p}{(dV_m)^2}$$

Because the mathematicians have gotten into the habit of not writing the parentheses, we eventually wound up with writing the short-hand notation, $\frac{d^2p}{dV_m^2}$, and since it is easier to write, that is the way it is written in most math textbooks.

Differentiating by calculator or by power rule, yields:

1ˢᵗ derivative: $\frac{dp}{dV_m} = -\frac{RT}{(V_m-b)^2} + \frac{2a}{V_m^3} = 0$ (1st derivative equals zero at critical points)

2ⁿᵈ derivative: $\frac{d^2p}{dV_m^2} = \frac{2RT}{(V_m-b)^3} - \frac{6a}{V_m^4} = 0$ (2nd derivative equals zero at points of inflection)

Since it is a pain to solve, I just used a CAS software to do it. The proof works, because the critical point is, in a calculus sense, a critical point, in that the slope at the point is zero. Thus, the first derivative is zero. Also, as seen on the graph of the isotherms, the special critical point is also a point of inflection, thus the concavity changes here. Therefore, the second derivative is also zero. The critical properties are as follows:

$$p_c = \frac{a}{27b^2} \qquad V_{m,c} = 3b \qquad T_c = \frac{8a}{27Rb}$$

Therefore, the critical properties of a gas described by the van der Waals equation can be found for a specific gas if we know the constants a and the b.

The Critical Compression Factor

From the critical constants, we can calculate the critical compression factor. Since Z includes the factor V_m, we can replace V_m with RT/p, because of the molar form of the ideal gas equation, $pV_m=RT$. From this, we can substitute back in. Thus,

$Z = \frac{V_{m,\text{real gas}}}{V_{m,\text{ideal gas}}}$ becomes $Z = \frac{V_{m,\text{real gas}}}{RT/p}$, which simplifies to $Z = \frac{pV_{m,\text{real gas}}}{RT}$. Our compression factor at the critical point is equal to:

$$Z = \frac{p_c V_{m,c}}{RT_c} = \frac{3}{8}$$

Although we get a value for the critical compression factor, this is an approximation, because the entire equation of state is an approximation. The value for most real gases is about 0.3, but the approximation is quite precise because the deviations are usually very small.

An Equation for Real Gases: $pV_m=RTZ$

We also get another interesting relation through this derivation. Since $Z = \frac{pV_{m,\text{real gas}}}{RT}$, we can rearrange the equation to result in $pV_{m,\text{any gas}} = RTZ$. For an ideal gas, Z is equal to one, and the equation is the same as the ideal gas equation. However, the equation still holds, for non-ideal gases, because the Z factor compensates for any deviations.

Equation for Corresponding States of van der Waals Gases

Reduced Variables

Another important idea that can be demonstrated through the application of the van der Waals equation is the principle of corresponding states. The principle of corresponding states is an approximation that allows us to write a similar equation of state, eliminate the factors that are specific to the equation (in this case, the a and the b), along with gas-specific values such as the critical constants, and replace them with the experimental conditions. The principle of corresponding states relies upon the critical conditions, and works well for spherical, nonpolar gases. For polar gases, or asymmetric molecules, it quickly falls apart because of attractive interactions. It is called the principle of corresponding states because through the principle, we

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws

can relate the state of one gas to the state of another. Instead of using the measured conditions directly, we divide these conditions by the conditions of the critical state. Thus, we obtain something called the reduced variables of the system. Reduced means that the value has been divided by a constant to fit it to some scale. The process of reducing is synonymous with normalizing. Thus, we do as follows:

$$p_r = \frac{p}{p_c} \qquad V_r = \frac{V_m}{V_{m,c}} \qquad T_r = \frac{T}{T_c}$$

If the reduced pressure, volume, and temperature are the same for two gases, then they are said to be in corresponding states. Corresponding states are expected to exhibit similar behavior.

Substituting Reduced Variables Into the van der Waals Equation of State

Now, we demonstrate it on the molar van der Waals equation, by substituting the values into the equation. The p is equal to $p_r p_c$, the V_m is equal to $V_r V_{m,c}$, and the T is equal to $T_r T_c$. Thus, we get the following:

$$p = \frac{RT}{(V_m - b)} - \frac{a}{V_m^2} = p_r p_c = \frac{R(T_r T_c)}{(V_r V_{m,c}) - b} - \frac{a}{(V_r V_c)^2} = \frac{R(T_r T_c)}{(V_r V_{m,c}) - b} - \frac{a}{V_r^2 V_{m,c}^2}$$

We still have the a and the b, along with three critical constants! However, we can now remove the critical constants if we express the critical constants in terms of a and b. Then, we find that the a and b term on both sides cancel out, leaving us with an equation purely based upon the reduced variables.

$$p_r p_c = \frac{R(T_r T_c)}{(V_r V_{m,c}) - b} - \frac{a}{V_r^2 V_{m,c}^2} = p_r\left(\frac{a}{27b^2}\right) = \frac{\left(\frac{8a}{27Rb}\right) RT_r}{(3bV_r - b)} - \frac{a}{(3b)^2 V_r^2}$$

$$= \frac{8aT_r}{27b(3bV_r - b)} - \frac{a}{9b^2 V_r^2}$$

This can then be simplified as follows:

$$p_r\left(\frac{1}{27b^2}\right) = \frac{8T_r}{27b(3bV_r - b)} - \frac{1}{9b^2 V_r^2}$$

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws

$$p_r\left(\frac{1}{27}\right) = \frac{8T_r}{27(3V_r - 1)} - \frac{1}{9V_r^2}$$

$$p_r\left(\frac{1}{1}\right) = \frac{8T_r}{(3V_r - 1)} - \frac{3}{V_r^2}$$

$$p_r = \frac{8T_r}{(3V_r - 1)} - \frac{3}{V_r^2}$$

And we are done with the derivation. When we graph p_r versus V_r isotherms for many gases, we find that they produce the same isotherms. The graph of the reduced isotherms of one gas describes that of many different similar gases, because the reduced isotherms of all van der Waals gases is the same. Likewise, all of the isobars, isochores, et cetera are identical, because the reduced behavior of all the van der Waals gases is the same, and the compression factor for corresponding reduced states is also roughly the same. This is what we call normalization of the data. We make the experimental data fit our model, to make calculations easier. Now, we can calculate with the reduced variables, and if we want the real variables, we can just plug in the real data to get a physically significant result. The van der Waals equation is not the only equation that can undergo this type of process. In fact, we do it quite frequently. However, it is just very easy to demonstrate on this historically significant equation.

The Virial Equation of State

Another historically significant equation is the virial equation of state. Its name comes from the Latin word vis, which means force, or energy. In the Latin times, force was thought to be the same as energy, so they called both vis. We know better now. The virial equation of state is another approximation. However, you can see the power series expansion on the right side. The series helps us approximate the behavior of the gas. It has infinite terms, and when we know the infinite number of constants that correspond to each term, it describes the given gas perfectly. The constants are called virial coefficients, and they can be found experimentally. However, it is a pain to find all these constants, especially because the virial coefficients change with temperature. Thus, the virial equation is mainly applied theoretically in proof-writing. It can be written in many ways, and the formulation of the equation was pioneered by Rudolf Clausius in 1870.

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws

The Thiesen Equation

In 1885, Max F. Thiesen, in his "Untersuchungen über die Zustandsgleichung," proposed that the state of a gas of a known density δ can be written as follows:

$$p = RT\delta(1 + T_1 d + T_2 d + T_3 d + \cdots)$$

He was the first to express an adaptation of the ideal gas equation in the type of series expansion form as above. His coefficients were based of the absolute temperature of the gas. However, the expression is difficult to use.

The Kamerlingh Onnes Equation

In 1901, Heike Kamerlingh Onnes proposed that the compression factor is related to the state of real gases as follows:

$$Z = \frac{pV_m}{RT} = \left(1 + \frac{C_1'}{V_m} + \frac{C_2'}{V_m^2} + \frac{C_3'}{V_m^3} + \cdots\right)$$

This is known as the Kamerlingh Onnes equation, which was included in his publication "Expression of the equation of state of gases and liquids by means of series." We can rearrange it to obtain the virial equation in its most commonly used form:

$$pV_m = RT\left(1 + \frac{C_1'}{V_m} + \frac{C_2'}{V_m^2} + \frac{C_3'}{V_m^3} + \cdots\right)$$

We write the virial equation in two ways is to make proof writing easier. Since p and V_m are related inversely, we can also write the equation as follows:

$$pV_m = RT(1 + C_1 p + C_2 p^2 + C_3 p^3 + \cdots)$$

The Ursell Equation

Later on, Harold Douglas Ursell applied the equation to statistical mechanics. His most notable paper on the topic is "The evaluation of Gibbs' phase-integral for imperfect gases," published in 1927.

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws

Properties of Virial Constants

Note the prime symbol, $'$, above the constants. The constants for the two different ways to write it are different, because the relation $pV_{\mathrm{m}}=RT$ does not hold perfectly for real gases. Thus, the constants need to all be determined experimentally. Usually, knowing the first three or four constants provides a very good approximation of the behavior of the gas, as long as the gas is not subjected to extreme conditions. Note that each factor has decreasing influence on the value of the overall series, as the terms become smaller and smaller. Usually, molar volume is far greater than 1, thus dividing by successive powers of the molar volume makes the later terms insignificant. Thus, the influence of the first few terms greatly overwhelms the terms that come after them in most circumstances. However, if the pressure is very large, or the density very small, thus leading to a small molar volume, the virial equation fails, and becomes wildly inaccurate. That would be the case of a liquid, or a supercritical fluid, which cannot be described by equations formulated for gases.

Approaching Ideality

We can obtain some interesting results from the virial equation. If all the virial coefficients are zero, we obtain the molar ideal gas equation. The equation also becomes like the ideal gas equation if the pressure goes to zero, or the volume goes to infinity. However, a real gas at low pressure and high temperature that can be described by the virial equation does not necessarily behave the same way as an ideal gas. Although the behavior of a real gas becomes close to that of an ideal gas in the limiting case, there is another special situation. Previously, we talked about the compression coefficient Z. We also found the relation $pV_{\mathrm{m}}=RTZ$. For an ideal gas, the Z is equal to one. Also, for an ideal gas, the power expansion on the right side of the virial equation is equal to one. Being that the two forms are equal, it is sometimes convenient to write it in the following way:

$$\frac{pV_{\mathrm{m}}}{RT} = Z = \left(1 + C_1 p + C_2 p^2 + C_3 p^3 + \cdots\right) = \left(1 + \frac{C_1'}{V_{\mathrm{m}}} + \frac{C_2'}{V_{\mathrm{m}}^2} + \frac{C_3'}{V_{\mathrm{m}}^3} + \cdots\right)$$

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws

Here, p needs to be zero for Z to become the ideal gas value of 1, and V_m likewise needs to be infinitely large for Z to equal 1. However, at low pressures and high volumes, we also know that since the two forms of the virial equation involve series with higher powers of p and V_m, the terms after the second term become nearly zero.

Special Conditions for Approximately Ideal Behavior

The criteria for ideality helps us find our special condition, which occurs at the Boyle temperature, T_B. Although Z approaches one when the pressure approaches zero and the volume approaches infinity, different gases approach the limiting conditions at different rates at different temperatures. Thus, the gas only behaves ideally for a small set of pressures and molar volumes. However, at the Boyle temperature, the gas described behaves nearly ideally, because the compression factor is nearly constant as we approach our limiting conditions. This allows for a much larger set of pressures and molar volumes for which the gas exhibits ideal-like behavior.

The first criterion is already stated, that we require low pressure and high molar volume. The second criterion is that the second virial coefficient, the most important coefficient after the one, goes to zero. We have already said that the compression factor of an ideal gas is a constant 1. When the second virial coefficient is zero, the entire expansion is very close to having a Z value of one. At the Boyle temperature, the gas behaves the most ideal, because the compression factor is close to one, and does not significantly change. What this also means is that the compression factor is not significantly affected by changes in pressure and molar volume.

Finding the Boyle Temperature for the Virial Equation

To find the Boyle temperature, we do the following. I will simultaneously apply the process to both ways that we wrote the virial equation.

First, we differentiate. Differentiation allows us to isolate the second virial coefficient.

$$pV_m = RTZ$$

$$pV_m = RT(1 + C_1 p + C_2 p^2 + C_3 p^3 + \cdots) = RT\left(1 + \frac{C_1'}{V_m} + \frac{C_2'}{V_m^2} + \frac{C_3'}{V_m^3} + \cdots\right) = RTZ$$

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws

$$(1 + C_1 p + C_2 p^2 + C_3 p^3 + \cdots) = \left(1 + \frac{C_1'}{V_m} + \frac{C_2'}{V_m^2} + \frac{C_3'}{V_m^3} + \cdots\right) = Z$$

$$\frac{dZ}{dp} = C_1 + 2C_2 p + 3C_3 p^2 + \cdots$$

$$\frac{dZ}{d\left(\frac{1}{V_m}\right)} = C_1' + \frac{2C_2'}{V_m} + \frac{3C_3'}{V_m^2} + \cdots$$

Then, we apply our limiting conditions. This allows us to neglect the rest of the terms of the expansion.

$$\lim_{p \to 0} \frac{dZ}{dp} = C_1 + 2C_2 p + 3C_3 p^2 + \cdots \cong C_1$$

$$\lim_{\frac{1}{V_m} \to 0} \frac{dZ}{d\left(\frac{1}{V_m}\right)} = \lim_{V_m \to \infty} \frac{dZ}{d\left(\frac{1}{V_m}\right)} = C_1' + \frac{2C_2'}{V_m} + \frac{3C_3'}{V_m^2} + \cdots \cong C_1'$$

We Use Z to Assist Us

We see that in the limiting cases presented, the derivative of the compression constant with respect to a variable that specifies the condition of the system is approximately the second virial coefficient. Since the first term is one, if the second virial coefficient is zero, the compression factor remains very close to one if we change the conditions slightly. At the Boyle temperature, the gas behaves the most ideal because the compression factor is close to one and does not significantly change. We have already said that the compression factor of an ideal gas is a constant 1. What this also means is that the compression factor is not affected by changes in pressure and molar volume. Thus,

$$\frac{dZ}{dp} \cong \frac{dZ}{d\left(\frac{1}{V_m}\right)} \cong 0 \approx \frac{dZ}{dV_m}$$

Since the virial coefficients of a gas depend on the temperature, we can proceed to find a temperature that makes the second virial coefficient equal to zero. That will ensure that Z is approximately one, and does not change when we slightly change the pressure and molar

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws

volume. At the Boyle temperature, the gas behaves almost as if it was an ideal gas. The Boyle temperature is also determined experimentally, and varies from gas to gas.

For a real gas:

$$\frac{dZ}{dp} = \frac{dZ}{dV_m} = \frac{dZ}{d\left(\frac{1}{V_m}\right)} \cong C_1 \cong C_1{}' \cong 0$$

Finding the Boyle Temperature for a van der Waals Gas

Going back to the van der Waals equation of state, we find that we can also expand it out in a power series fashion, just like the virial equation of state, which is a power series expansion of the ideal gas equation of state. Thus, we can mathematically approximate the Boyle temperature for a van der Waals gas. We start from the molar form of the van der Waals equation of state:

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

A Series Expansion

We rearrange the equation into a form that we can expand using the following binomial expansion which is valid for x<1:

$$\frac{1}{1-x} = 1 + x + x^2 + \cdots$$

It will result in an equation very similar to the virial equation.

We rewrite the molar form of the van der Waals equation as follows:

$$p = \frac{RT}{V_m}\left(\frac{1}{1 - \frac{b}{V_m}}\right) - \frac{a}{V_m^2}$$

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws

As long as $\frac{b}{V_m} < 1$, we can use the expansion shown before, by treating $\frac{b}{V_m}$ as x in the series expansion. Since b is usually very small, and V_m is usually fairly large, $\frac{b}{V_m}$ is usually far smaller than 1. So, we expand using the series and rearrange the equation again:

$$p = \frac{RT}{V_m}\left(1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \cdots\right) - \frac{a}{V_m^2}$$

We are not yet done. We need to move the $-\frac{a}{V_m^2}$ term inside the expansion.

$$p = \frac{RT}{V_m}\left(1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \cdots - \frac{V_m a}{RTV_m^2}\right)$$

$$p = \frac{RT}{V_m}\left(1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \cdots - \frac{a}{RTV_m}\right)$$

$$p = \frac{RT}{V_m}\left(1 + \frac{b}{V_m} - \frac{a}{RTV_m} + \frac{b^2}{V_m^2} + \cdots\right)$$

$$p = \frac{RT}{V_m}\left(1 + \frac{\left(b - \frac{a}{RT}\right)}{V_m} + \frac{b^2}{V_m^2} + \cdots\right)$$

Our result looks VERY similar to the virial equation. In fact, it looks almost the same as the virial equation! Therefore, we are going to try to find the Boyle temperature of a van der Waal gas.

We Use Z to Assist Us

We know $pV_m=RTZ$ and $Z = \frac{pV_m}{RT}$. Therefore, we know from above, that:

$$Z = \frac{pV_m}{RT} = \left(1 + \frac{\left(b - \frac{a}{RT}\right)}{V_m} + \frac{b^2}{V_m^2} + \cdots\right)$$

We see that the first term of the expansion that equals the compression factor is 1, and that each term following the 1 decreases significantly in size. This allows us to perform the same type of procedure as we did before, which is setting the second power expansion coefficient equal to

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws

zero. However, we do not need to differentiate, as we are given the value of the second virial coefficient. Thus, for conditions where volume is very large, we just need to set the coefficient equal to zero, and then solve for T. I will still show the derivative below, to show that when volume is large, the second coefficient is approximately the change in Z with respect to the inverse of volume:

$$\frac{dZ}{d\left(\frac{1}{V_m}\right)} = \left(b - \frac{a}{RT}\right) + \frac{2b^2}{V_m} + \cdots$$

For the Boyle temperature:

$$0 = \frac{dZ}{d\left(\frac{1}{V_m}\right)} = \left(b - \frac{a}{RT}\right) + \frac{2b^2}{V_m} + \cdots$$

$$0 = \lim_{\frac{1}{V_m} \to 0} \frac{dZ}{d\left(\frac{1}{V_m}\right)} = \lim_{V_m \to \infty} \frac{dZ}{d\left(\frac{1}{V_m}\right)} = \left(b - \frac{a}{RT}\right) + \frac{2b^2}{V_m} + \cdots$$

$$0 = \lim_{\frac{1}{V_m} \to 0} \frac{dZ}{d\left(\frac{1}{V_m}\right)} = \lim_{V_m \to \infty} \frac{dZ}{d\left(\frac{1}{V_m}\right)} \approx b - \frac{a}{RT}$$

Thus, solving for the T, which in this case is T_B, we get:

$$b - \frac{a}{RT_B} = 0$$

$$b = \frac{a}{RT_B}$$

$$T_B = \frac{a}{Rb}$$

Critical Constants, van der Waals Constants, and the Boyle Temperature

Therefore, if we know the van der Waals coefficients, we can find the Boyle temperature. The expression for the Boyle temperature can be further rearranged, for us to be able to calculate

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws

the Boyle temperature if we know another special temperature, the critical temperature, for the gas.

From way long ago, we had: $T_c = \frac{8a}{27Rb}$. Rearranging, and multiplying, we get:

$$T_B = \frac{a}{Rb} = \frac{27}{8}\frac{8}{27}\frac{a}{Rb} = \frac{27}{8}T_c$$

Now, for a van der Waals gas, if we know the critical temperature, we know the Boyle temperature as well! Although it seems that we have a concrete result, unlike what we obtained for the Boyle temperature for a gas described by the virial equation of state, note that both requires experimentation. For the Boyle temperature found from the virial equation, we need to experimentally determine the temperature. Same here, where we have to determine a temperature experimentally. For a real gas, it is pretty much impossible to determine physical or chemical constants without hitting the lab and doing some form of experimenting or another.

Chapter 4: Limits to Ideal Gas Behavior, and Other Gas Laws

Chapter 5: Thermodynamics

The Zeroth Law of Thermodynamics, and the Measurement of Temperature

Feeling Hot or Not

Sensing hot and cold using your skin is not a very reliable way to measure temperature. This is because our sense of hotness and coldness is relative, and only measures how fast heat is taken away or transferred to our skin. Nothing makes things cold. Coldness is just a lack of heat, just like how low pressure is simply a lack of pressure.
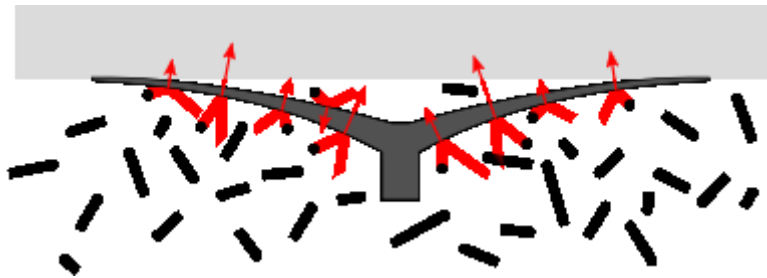
Figure 5.1. A diagram of a suction cup, showing that pressure is relative. Heat is also relative, in that a lack of heat is sensed as lower content in heat, or "cold."

So, it will make sense that heat-rich hotter things, called heat sources, will give heat to heat-lacking colder things, called heat sinks.

Heat transfer is quicker when there is a greater difference in temperature between the hot object and the less hot object. That is the reason why hotter things feel hotter than relatively less hot things, because the heat is simply being transferred to our skin more quickly in the case of the hotter thing. The same applies for cold things, except now you are the hot object. Nothing makes things cold. Since in both cases the amount of heat given by the heat source and the amount of heat received by the heat sink are the same, coldness just means that the object (the heat sink) is taking heat away from you (the heat source).

The cases above are explained, with the assumption that the objects are all made of the same material. However, here comes the real inaccuracy. Different materials transfer heat at different rates. Therefore, on a cold day, if you touch a metal surface, it will feel colder than a wooden surface, although both are at the same temperature! You can verify this by using a

thermometer. This tells us that metal is a better conductor than wood, in that it can transfer heat faster. Thus, we find that feeling with the skin is a terrible way to measure the actual temperature of an object. Instead, we need a thermometer.

The Invention of the Thermometer

Although humans have associated temperature with hot or cold for thousands of years, the notion of temperature was not well defined until the 1700's. Galileo Galilei's invention of the thermoscope in 1593 and the thermometer in 1603 gave quantitative meaning to the word temperature.
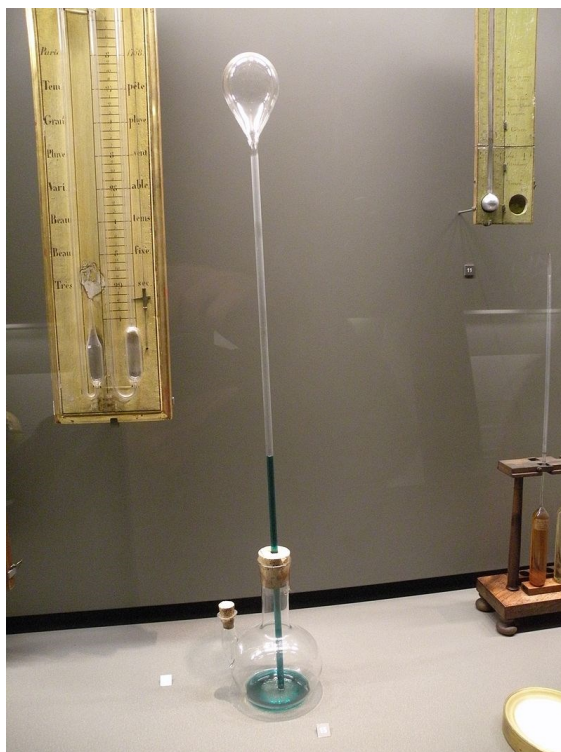
Figure 5.2. A Galileo thermoscope.

It allowed humans to quantitatively describe something that we could previously only estimate qualitatively. The idea of measuring temperature is based off of a very fundamental principle, which we call the zeroth law of thermodynamics. It is so fundamental that it comes before the first, because if the zeroth law does not hold, then measuring temperature is just as good as licking the car mirror during a blizzard. The zeroth law says that if object A is at the

Chapter 5: Thermodynamics

same temperature as object B, and object B is at the same temperature as object C, then object A and C are at the same temperature. The concept might sound simple, but it is absolutely necessary to know.

From Early Theories of Heat to the First Law of Thermodynamics

People have been going around making theories about heat for at least 2500 years. In 485 BCE, Parmenides hypothesized in his book *On Nature*, that there was a substance named primum frigidum that was responsible for making things cold. There were also many similar, less famous theories. Although Galileo Galilei proposed a relatively modern atomistic theory of heat in 1623, it did not become widespread, and the advancement described in *Il Saggiatore* was postponed for another 200 years. The next major theory of heat came in 1667, when Johann Joachim Becher proposed that there was a substance called terra pinguis that flows when things burn. The theory was mainly based in alchemy, and does not correspond well to observation. However, the idea became popularized as the phlogiston theory in 1703, when Georg Ernst Stahl proposed a similar theory, in which Becher's terra pinguis was renamed phlogiston.

Amontons and Absolute Zero

In 1702, Amontons used a J-tube thermometer, and his law relating temperature and pressure, to extrapolate that there was a temperature at which the volume and pressure of a gas is zero. He was the first to conclude that there may be a temperature that we cannot go below. According to his law, going below that point, which we set as zero, results a physically impossible result such as negative pressure or volume. Amontons' estimate of -240 degrees below the freezing point of water is very close to the modern accepted value of -273.15 degrees Celsius, thus making him the first to establish a gas-based absolute temperature scale. Again, we return to the extrapolation that we have seen before:

Chapter 5: Thermodynamics
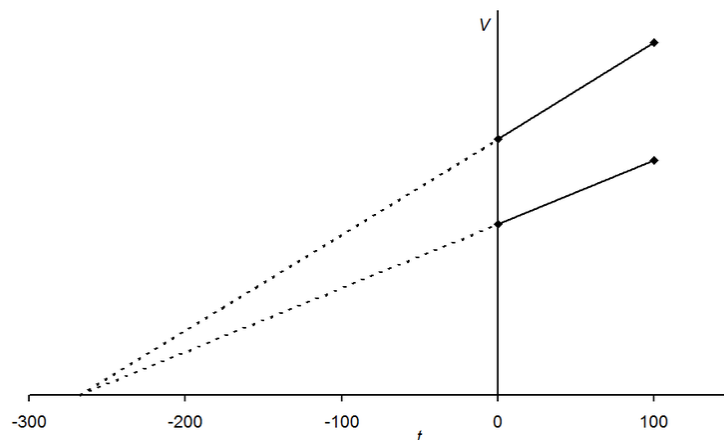
Figure 5.3. An extrapolation using 2 lines to find absolute zero, using volume and temperature. The same can be done for a graph of pressure and temperature.

The Celsius Scale

The Celsius scale was not invented until 1742, when Anders Celsius, the thermometer maker, established his scale of temperature. Unlike the modern Celsius scale, Anders Celsius set 100 degrees as the freezing point of water, and zero degrees as the boiling point of water at sea level. Celsius knew that the boiling point of water varies with atmospheric pressure, and the relation between the two is named after him. To allow for easy and accurate calibration, he recommended that the boiling point be calibrated at sea level, where atmospheric pressure is rather constant. The Celsius scale used to be called the centigrade (hundred steps) scale, because he divided the temperature between the boiling and freezing points of water into a hundred subdivisions. Good friends wait for each other when going places. To make life easier, Carl Linnaeus waited for his good friend Celsius to be located six feet under ground level. That happened in 1744, and Linnaeus made Celsius flip upside down. We now have zero degrees Celsius as freezing, and a hundred degrees Celsius as boiling, which is far more practical than the original configuration.

Origins of the Caloric Theory

Then, in the 1770s, after performing numerous calorimetry experiments, Antoine Lavoisier proposed the exact opposite of the primum frigidum theory. Because the phlogiston

Chapter 5: Thermodynamics

theory is completely nonsense, he proposed that there was a massless fluid, caloric, that was responsible for making things hot. The caloric theory of heat was an improvement over the primum frigidum theory of heat, because it identified that sources of heat exist, but not sources of cold. Thus, the caloric theory explained that hot objects have more of something than cold objects. He included in the theory that caloric (heat) flows, similar to phlogiston, and that caloric is conserved. This is one step closer to the conservation of matter. As time proceeded, conservation of caloric developed into conservation of heat, which in turn developed into the conservation of energy in general, and the conservation of energy was eventually unified with the conservation of mass to form the principle of conservation of matter. Although the caloric theory has its weaknesses, it provided some basis of measuring what was not defined earlier, and was temporarily good enough for scientific development in the next thirty years or so.

Another Extrapolation for Absolute Zero

In 1777, Johann Heinrich Lambert completed his *Pyrometrie* four months before his death. He had conducted some experiments extrapolating the relation between pressure and temperature. His experiments were very similar to Amontons' earlier experiments, and he also concluded that there was an absolute zero temperature that forms the basis of the absolute temperature scale. His value of absolute zero had less than ten percent of the error that Amontons had. Lambert extrapolated absolute zero to be at about -270 degrees Celsius. By this point, the Celsius scale had already existed for thirty years.

Disproving the Caloric Theory

Lavoisier's caloric theory of heat does not explain some things. Although it explains combustion as a release of trapped caloric, it really breaks down when attempting to explain the relationship between work and heat. For example, if you rub two sticks together, the two sticks become hot, even though the sticks are not on fire yet. Since Lavoisier's theory of heat includes conservation of caloric, it is very difficult to explain where the extra caloric come from. That is when the caloric theory falls apart. Theories become invalid when they are not consistent with the observed.

Chapter 5: Thermodynamics

Count Rumford's Conversion of Work to Heat

While observing soldiers bore a cannon, Benjamin Thompson aka Count Rumford found that massive amounts of heat were produced by friction. Rumford set up an experiment, in which a single horse boring a cannon boiled 27 pounds of ice in two and a half hours. His 1798 publication, "An Experimental Enquiry Concerning the Source of the Heat which is Excited by Friction," described the process. He proceeded to also prove that the metal bored out of the cannon and the cannon were made of the same material by providing specific heat measurements.
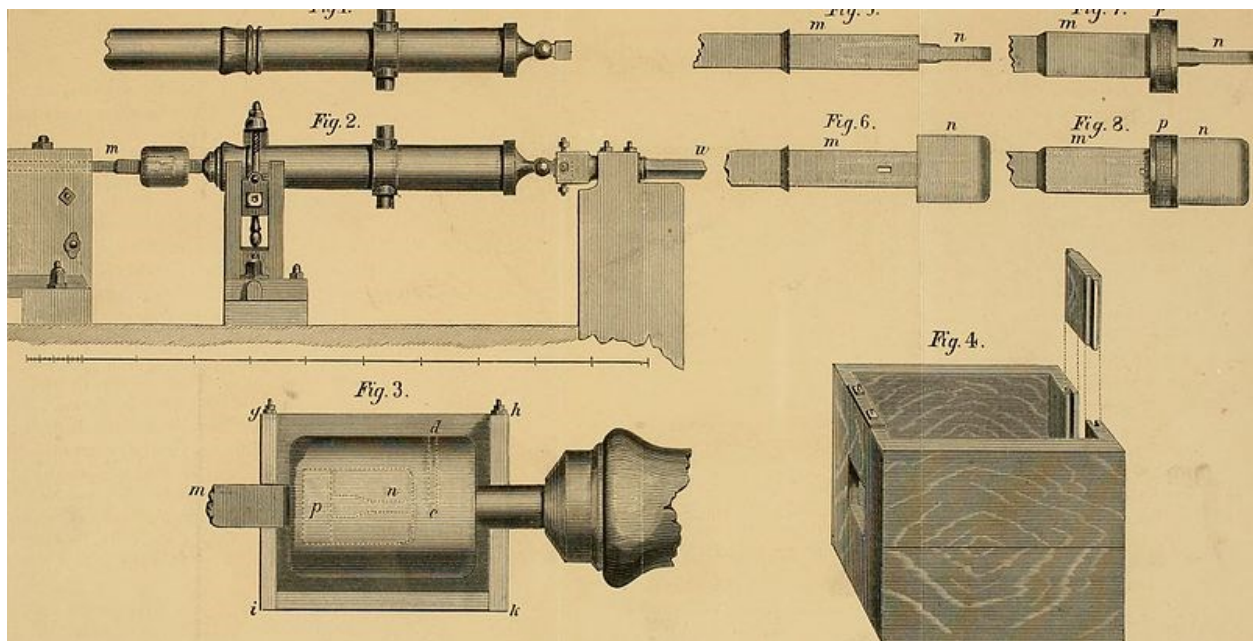
Figure 5.4. Count Rumford's setup to measure the amount of heat produced during the process of boring a cannon.

For Rumford, who was highly educated in the contemporary sciences, his results were obvious violations of the conservation of caloric proposed by Lavoisier, because "extra" caloric appeared to appear from no reasonable source other than the only thing transferred to the cannon, which is motion. Despite the evidence that strongly refutes the belief that heat cannot be created, the caloric theory was not disproved in the eyes of the public until the 1840s, because scientists at the time believed that the caloric theory could be adjusted to fit the exception, and that Rumford was not precise enough in his experiment. Also, scientists at the time knew that

Chapter 5: Thermodynamics

electricity can also be generated by friction, and they believed that electricity was also a fluid that flowed from one object to another.

Pictet's Experiment, and Frigoric

Even with the notion of absolute zero, some still believed that there was another fluid similar to caloric, called frigoric, which was responsible for coldness. In the late 1780s, Marc-Auguste Pictet performed an experiment with Horace-Benedict de Saussure, in which they discovered infrared radiation. By this point, they knew that heat can travel through space as a form of radiation that can be focused by mirrors. Pictet then proceeded to use concave mirrors to focus the radiation from hot and cold sources onto an air thermometer. Pictet found that when he placed a hot object on the focal point, the thermometer indeed heated up, because the infrared radiation from the hot object was reflected onto the thermometer. This increased the temperature, as indicated by the thermometer. However, when he placed a cold object at the focal point, the temperature of the thermometer cooled down. The results were published in Pictet's 1790 "Essai sur le feu" (An Essay on Fire). There seemingly was some form of radiation that was responsible for cooling, and Rumford interpreted the results of Pictet's experiment as evidence of his frigorific rays. Rumford believed that hot and cold resulted from vibrations in a nonexistent substance called aether. However, we now know that this conclusion was incorrect, and that aether is nonexistent. Although Pictet performed the experiment correctly and got valid results, it was difficult to interpret the data at the time. Despite his results, Pictet had already become a supporter of Lavoisier's theory, and he was convinced that there was no frigoric.
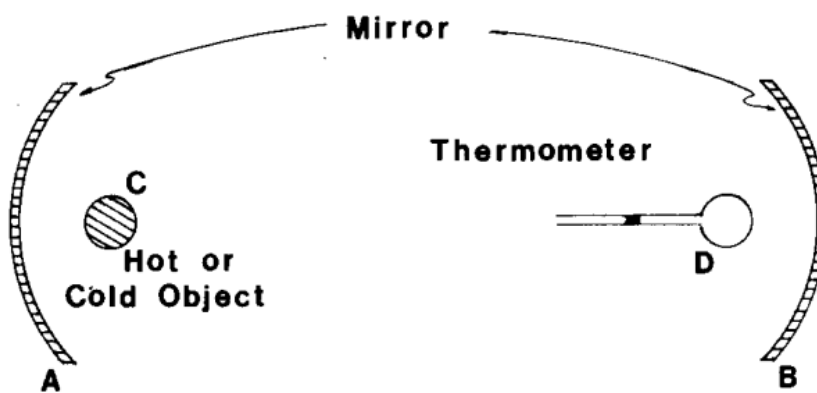

Figure 5.5. A diagram of Pictet's experimental setup.

Chapter 5: Thermodynamics

Prévost's Explanation of Pictet's Results

Eventually, in 1791, Pierre Prévost proposed in his landmark paper, "Mémoire sur l'Equilibre du feu," that all things radiate heat, and that nothing radiates cold regardless of how not hot it is. He continued his research on thermal radiation, and in 1809, he wrote his "Du Calorique Rayonnant." Even if we do not visibly see the heat being radiated as light, blackbody radiation still occurs if the body has a temperature above absolute zero. We now know that Prévost is correct, and that there is nothing that is responsible for making things cold. Modern thermodynamics define coldness as the lack of heat. Pictet's experiment is very interesting. If nothing radiates cold, then why do the concave mirrors appear to reflect cold? We can now explain this by applying Prévost's theory, and observe that the thermometer radiates heat at a relatively constant rate. However, the environment also radiates heat. The temperature of the thermometer does not change if the amount of heat it absorbs is the same as the amount of heat it radiates. When there is a hot object, the hot object radiates heat, which increases the temperature reading on the thermometer. When a thermometer is put in a room, it radiates just as much heat as it absorbs from the room. However, when the thermometer is at a focus of a concave mirror without a significant heat source, the concave mirror blocks enough of the heat that the room emits, which makes the thermometer lose more heat than it absorbs. The same effect is used to make refrigerators in areas with no electricity. An inverted solar cooker shades the object at its focus from infrared radiation that originates from the surroundings. This allows the object to radiate more heat to the surroundings than it absorbs, thus cooling down the object. The same principle is applied when you cool down by sitting in the shade.
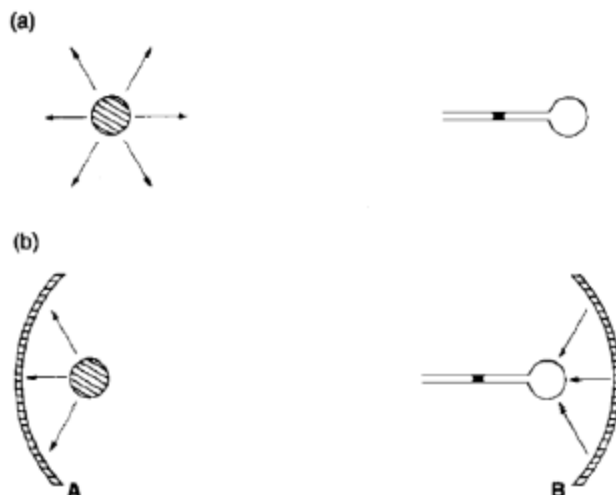
Chapter 5: Thermodynamics

Figure 5.6. A diagram of the rays originating from the hot object which are reflected to the thermometer. First, the rays are emitted. Then, they are reflected from the mirror closer to the object to the mirror closer to the thermometer. Then, from the mirror closer to the thermometer, they travel to the thermometer, which increases the temperature of the thermometer. For the "cold" object, there is not much heat emitted, to be reflected towards the thermometer. Thus, although for both objects the mirror shades the thermometer from heat emitted from the surroundings, and the thermometer constantly radiates heat, the cooling effect may be observed for the object that lacks heat (which does not emit enough infrared radiation to mask the effects of the shading).
One important thing to notice, is that even if the supposed source of the fictitious "frigorific" rays was not present, the thermometer would still cool down, just like how objects can be cooled by placing them at the center of an inverted solar cooker.

Yet Another Extrapolation

In 1802, Gay Lussac published his law of temperature and pressure, and brought Charles' unpublished equation to public attention. Gay Lussac got even closer to the value of absolute zero, and his error was about than five percent of Lambert's! He used the number 273 in his gas law, to relate absolute zero to the freezing point of water. Thus, he was only .15 of a degree away from the modern accepted value!

The End for the Caloric Theory

In the 1840s, the caloric theory of heat was finally debunked, when the first law of thermodynamics, the conservation of energy, was established. Previously, in the late 1770s, there was already speculation as to the matter of what is caloric. In investigating combustion, which supposedly releases trapped caloric, Lavoisier and Laplace placed a guinea pig in an ice calorimeter.

Chapter 5: Thermodynamics
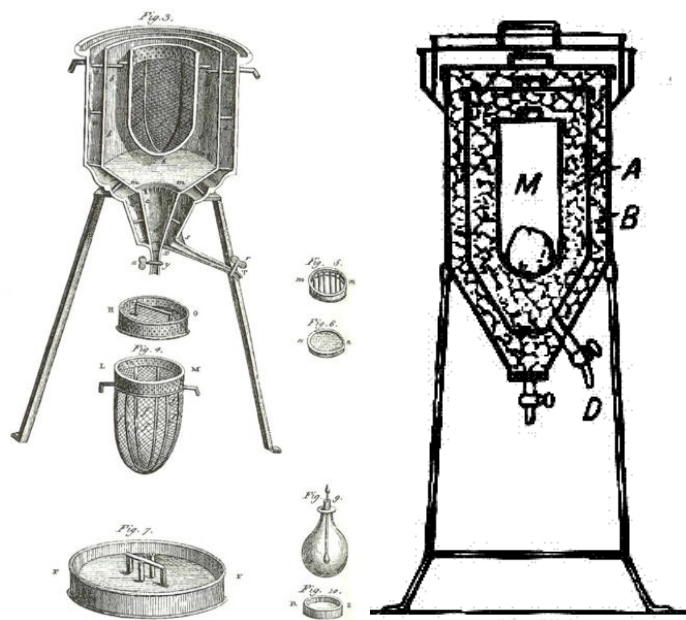
Figure 5.7. Two drawings of Lavoisier and Laplace's ice calorimeter. The guinea pig was placed at the center marked M, which was surrounded with ice. The amount of water from the melting ice, and the amount of CO_2 the guinea pig emitted was measured.

Since they already knew how much heat is required to melt ice, they can calculate how much heat the guinea pig gave off. Then, because they knew the amount of CO_2 gas that the guinea pig normally respired, they calculated that the amount of energy from the guinea pig that turned into heat is approximately equal to the amount of energy released by combustion, if a corresponding amount of CO_2 was produced. Thus, they concluded that the animal body liberated caloric from food through a process they deemed respiration, and hypothesized that the mechanism for respiration is similar to that of combustion. What they obtained from the experiment, but failed to realize, was an early form of the conservation of energy. Lavoisier believed in the conservation of caloric, and the conservation of mass. However, it took one step to arrive at the conservation of energy, because energy was not well understood at the time. Now, we know that the amount of heat released by the guinea pig in the experiment and the amount of heat from combustion is nearly exactly equal.

Chapter 5: Thermodynamics

The First Proposal of the First Law

In 1842, Julius Robert von Mayer established oxidation as the process that releases energy in all living things. He also calculated that mechanical and chemical energy, along with heat, are equivalent. He was rejected initially due to his lack of a formal background in physics. However, after heating water by vibration, and performing a series of calculations to prove that heat is the kinetic energy of molecules, his 1842 paper, "Remarks on the Forces of Inorganic Nature," was published. It contained the earliest statement of the conservation of energy. However, his lack of adeptness at promoting his discovery left the credit to James Joule, who arrived at the same principle one year later in 1843.

James Joule, and the First Popular Proposal of the First Law

James Joule, by the time of his discovery, had extensive experience with energy. He was initially in the engine industry, and was familiar with electric and coal power. Therefore, Joule had a substantial background in the field. It is also important to note that Joule was Dalton's student. Therefore, although some scientists did not believe in atoms and molecules, Joule was a firm supporter of the notion, and the concept assisted his ability to rationalize heat as the motion of those particles. Thus, he had an earlier suspicion that heat was only kinetic energy, but on the microscopic scale.

Joule began his search for an alternative theory of heat when he realized that electric components become hot due to transformation of electric energy to heat, and not from conduction from other components as explained by the caloric theory, which was accepted by scientists at the time. This effect is called Joule heating in his honor. Although the established mainstream theory disagreed with him, Joule was a master experimenter. Through a series of experiments, he proved that mechanical energy supplied to various objects can be directly converted to heat. Although he did some of his early experimental work by compressing fluids, he eventually performed his famous hallmark experiment.

Joule took a mass, attached it to a paddle using a pulley, and proved that when the mass fell, the gravitational potential energy of the mass was converted into kinetic energy of the paddle, which was converted to heat by drag. The earth did work on the mass, which did work on the pully, which did work on the fluid (water). Work, which was somewhat understood at the

Chapter 5: Thermodynamics

time due to classical mechanics, was known to be a means of transferring energy. In his experiment, drag, a form of resistance found in fluids, served the same purpose as friction in Rumford's experiment. Through his clever apparatus, he established the theory of the conservation of energy by proving that heat was indeed another form of energy, and that energy can exist and be converted into many forms.
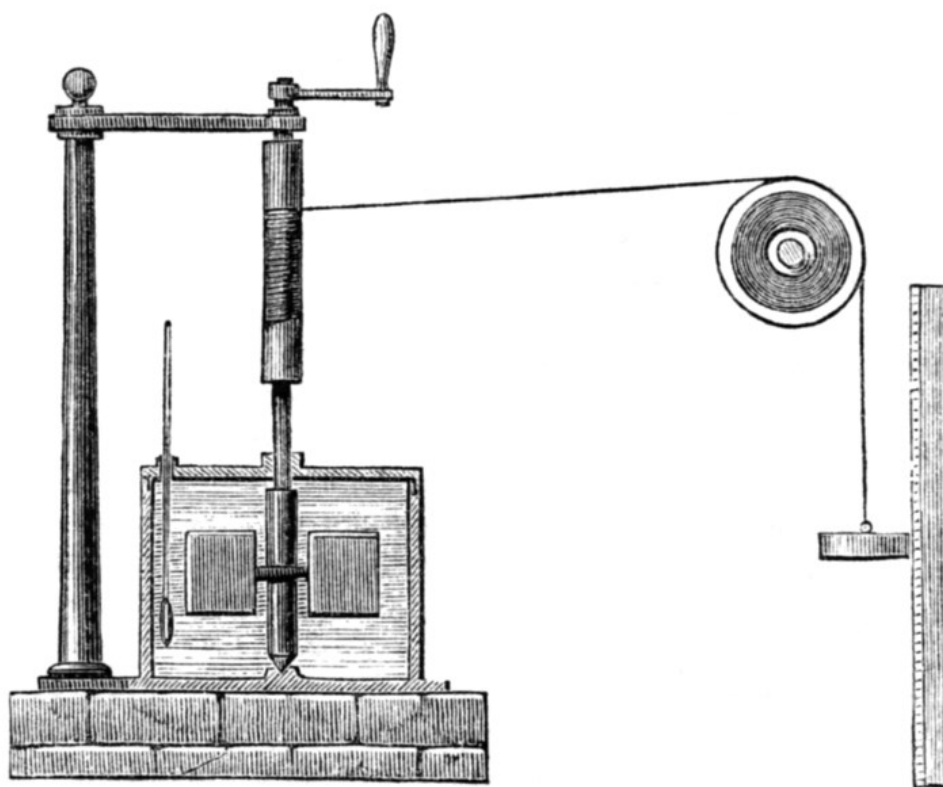
Figure 5.8. A diagram of Joule's experiment. The falling mass rotated the paddle, which warmed up the water, thus showing the conversion of mechanical energy into heat energy, and proving that heat and work are simply different forms of energy.

In 1847, Hermann von Helmholtz knew of the work of both Julius Robert von Mayer and James Joule when he wrote his "On the Conservation of Force." At the time, the same word was used for both force and energy, just like how vis was used for both force and energy in Latin. He credited both in his influential statement of the conservation of energy. Later on, from 1852 to 1856, Joule collaborated with William Thomson aka Lord Kelvin, and they discovered many other interesting effects such as the Joule effect, and the Joule-Thomson effect. Joule, as always, performed the experiments, and Thomson suggested further experiments and interpreted the

Chapter 5: Thermodynamics

results. Their discoveries eventually set the basis for the new kinetic theory, and Joule was given most of the credit far sooner than Mayer, who was institutionalized due to severe depression. The principle of conservation of energy is the first law of thermodynamics. Thus, perpetual motion machines of the first kind, which are based upon infinite energy, are impossible, because they break the first law of thermodynamics.

Hess's Law

A statement that is based upon the first law of thermodynamics is Hess's law, named after Germain Hess, who included it in his 1840 publication "Recherches thermochimiques." It says that summing up balanced thermochemical reactions results in more balanced thermochemical reactions. Thus, we can use two reactions to find a third, along with associated thermodynamic values for the third reaction. We will see applications of Hess's law later, when we discuss reactions. However, just note that all Hess's law means is that summing up the individual steps needed to achieve a final reaction results in the final reaction. What makes Hess's law especially useful, is that it allows us to investigate reactions that are impossible, or difficult to measure. Another application of Hess's law is to find the lattice enthalpy of an ionic substance, based upon tabulated standard reaction enthalpies. The cycle shown below is known as the Born-Haber cycle, named after its two inventors, and can be applied to any ionic crystal in the same manner as demonstrated on Lithium Fluoride.

Chapter 5: Thermodynamics
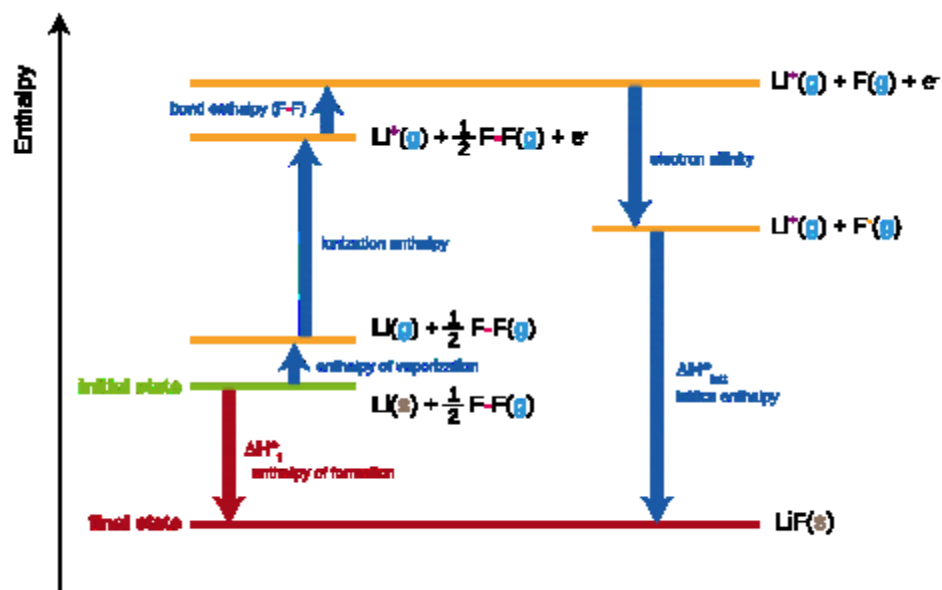
Figure 5.9. The Born-Haber cycle for finding the lattice enthalpy of LiF. The cycle is based upon the conservation of energy, and involves repeated applications of Hess's law.

The Modern Absolute Thermodynamic Temperature Scale

In 1848, Lord Kelvin published his idea of the infinite cold, in his "On an Absolute Thermometric Scale." His infinite cold is set at zero, and is another way of saying absolute zero. Using the temperature scale of the air thermometers available, he also resulted in Gay Lussac's value of negative 273 degrees Celsius, although he arrived at the value mathematically. Using the accepted gas expansion coefficient with respect to a degree Celsius, he found that the inverse of the gas expansion coefficient resulted in the value he sought after, which was absolute zero. At his time, the gas expansion coefficient was accepted to be 0.00366. Doing the inverse results in 273.22 degrees Celsius, which is less than 0.07 away from the modern accepted value of absolute zero. Therefore, he pioneered the first accurate absolute thermodynamic temperature scale, which is the same as the absolute ideal gas temperature scale. In 1859, William John Macquorn Rankine did virtually the same thing as Lord Kelvin. However, he used Fahrenheit degrees instead. This other Rankine scale is less useful, although some American engineers still hold onto it, much like how we hold onto the Fahrenheit scale.

Chapter 5: Thermodynamics

The Kinetic Molecular Theory of Heat

In the late 1870s and the early 1880s, heat was explained with a new model, the Kinetic Molecular Theory, which was mathematically established by Ludwig Eduard Boltzmann to describe thermodynamic processes on the microscopic scale. Boltzmann is the pioneer of statistical mechanics and modern thermodynamics. For the first time, thermodynamics was treated from a perspective on the molecular scale, rather than on the scale of the entire stochastic system. Boltzmann was the student of Joseph Stefan, a prolific physicist famous for deriving the mathematical equations describing black body radiation, and other pioneering laws and equations in a variety of other fields, such as electromagnetism, optics, thermodynamics, and the kinetic theory of heat. Not only did Stefan provide Boltzmann a strong introduction to the kinetic theory of gases, Stefan also introduced Boltzmann to recent advances made by James Clerk Maxwell, a pioneer in electromagnetism, the kinetic theory, thermodynamics, relativity, and quantum mechanics.

Various Statements of the Second Law

Lazare Carnot's Interpretation

The second and third laws of thermodynamics are all about this quantity called entropy. Entropy is a very simple idea, but the concept is very often difficult to describe. Entropy is a measurement of the possible amount of disorder in a system. One of the earliest description of entropy is the tendency of a system to dissipate useful energy. Thus, it is observed when friction stops cars, or when balls stop bouncing, or a host of other things. In fact, it is something that increases whenever something happens, and unlike the common logic that "what can be increased can be decreased," when entropy is increased it cannot be decreased. Thus, it tends to go to infinity, which so happens to correspond to when the system cannot do anything useful anymore. This definition was provided by Lazare Carnot in 1803, in his "Fundamental Principles of Equilibrium and Movement." He called entropy the loss of moment of activity, or the ability to do useful work. Carnot was an engine maker.

Chapter 5: Thermodynamics

Sadi Carnot's Interpretation

His son, Nicolas Léonard Sadi Carnot, continued his work. Sadi Carnot also made a statement that reflects upon the nature of the second law. He stated in 1824 that for engines that depend on heat, useful work is done when the heat falls through a potential difference, much like how water falls on a water wheel. This means that although heat is generally conserved based upon the first law of thermodynamics, as shown by Count Rumford, heat cannot be restored to original condition after it falls through the potential difference. Thus, an ideally efficient engine is impossible. The famously impossible Carnot engine, an example of an ideally efficient engine, was named after him, and is often used to illustrate the concept of the second law. The Carnot engine is an ideal model of a perpetual motion machine of the second class, in that it violates the second law of thermodynamics. Although the first law was not widely established until 1843, Sadi Carnot drew his conclusions in his "Reflections on the Motive Power of Fire" from the Newtonian hypothesis that heat and light are indestructible forms of matter that are conserved.

Rudolf Clausius' Classical Heat Engine Interpretation, and Clausius' Inequality

In the mid-18th century, Rudolf Clausius objected to the idea that energy is not changed when it is transferred. He mathematically deduced that when work is done, there are inevitable losses of energy, which cause a portion of the energy to no longer be useful. Rudolf described entropy as "transformation content," which means that heat becomes unavailable for doing work. In 1850, he issued his Clausius statement of the second law of thermodynamics, that heat cannot go from cold to hot without some investment of energy. Thus, leaving the refrigerator door open to cool down the room during the hot summer will only heat up the room. Of course, this was not instantly widely accepted, as heat was previously seen to consist of particles that are conserved. However, the Clausius statement quickly became very famous, as it was experimentally verified. In short, it means that there is this value that increases when any thermodynamic process occurs, and that the value measures the loss of energy to useful work. Mathematically, he wrote that for any process, a small increase in entropy is brought upon by a small amount of heat transferred at a given temperature:

$$\mathrm{d}S \geq \frac{đq}{T}, \text{where đ is just a very small } \Delta$$

Chapter 5: Thermodynamics

Thus, different paths lead to different increases of entropy, and none of the paths from state 1 to state 2 has less increase in entropy than an impossible reversible path, which has an increase in entropy of exactly $\frac{đq}{T}$. Also, notice that when the temperature gets bigger and bigger, the change in entropy is less and less, because a small amount of disorder is insignificant when there is disorder everywhere, and a small breeze cannot be noticed when there is a tornado. However, it is not possible to make the entropy go to zero by increasing the temperature, because there is supposedly a maximum temperature, after which physics do not hold anymore. That temperature, estimated to be at about 1.416833×10^{32} K, is called the Planck temperature. Another thing to note is that for a perfect crystal at 0 K, the addition of even a tiny amount of heat creates a very large amount of disorder. Thus, this is one of the reason why reaching very low temperatures is very difficult. The only way to minimize entropy is to do nothing. No processes, no change, no increase in entropy. However, as time passes, there is inevitably increase in entropy, no matter how hard we try to prevent it. Next time you are told to clean your room, just try to light the house on fire before you trash it, so that there is a less noticeable peculiarity for the house insurance company.

Lord Kelvin's Statement

In 1851, Lord Kelvin issued his Kelvin statement of the second law of thermodynamics, that dissipation certainly occurs when energy is transferred irreversibly. Since all real processes are irreversible, perpetual motion machines of the second kind that are based upon ideal reversible conservation of energy are impossible. They break the second law of thermodynamics, which is why the patent office strictly rejects all proposals regarding such mechanisms. Afterwards came Max Planck, who said that although entropy is increased during irreversible processes, entropy does not change in the case of impossible reversible processes. Thus, we see a pattern here, that a quantity called entropy increases when energy is transferred irreversibly, which makes the restoration of energy to its original state impossible. Entropy, in short, is the wastage of energy that occurs when energy becomes randomized and disorderly. Useful energy is orderly, and does what is intended. However, due to entropy, energy tends to become disorderly, which reduces its ability to do useful work. Later, the Kelvin statement and the Planck statement were combined to form the Kelvin-Planck statement, which prohibits engines

Chapter 5: Thermodynamics

that operate with 100% efficiency. All the above say virtually the same thing. However, notice that they all regard the special quantity, entropy, on the scale of systems.

A Change of Perspective: Statistical Mechanics

The Boltzmann Entropy Formula

Later, statistical mechanics was developed by Josef Stefan, Ludwig Boltzmann, Josiah Willard Gibbs, Hermann von Helmholtz, James Clerk Maxwell, and many other pioneers. In statistical mechanical terms, the amount of entropy in a system can be calculated using the Boltzmann entropy formula, which embodies the basic statistical definition of entropy. Boltzmann is important, because his work with Maxwell helped develop the Maxwell distribution, and the Maxwell-Boltzmann distribution, which set the foundation for the investigation of thermodynamics on the molecular scale. Statistical mechanics allowed for an entirely new set of interpretations for energy and heat. Entropy was also redefined when Boltzmann derived the probability-based equation for entropy, which is theoretically significant. The Boltzmann entropy formula relates how many microstates that a collection of molecules can occupy. Microstates are certain arrangements of the molecules in the system, spatially and energetically. In short, it states that the entropy depends on the probability that the particles occupied certain positions in certain orientations. This was the first equation to describe systems from the microscopic scale, hence microstates. The formula, which Boltzmann came up with in 1877, is as follows:

$$S = k\log(W), \text{where S is entropy}, \log \text{ is the natural logarithm},$$
$$k \text{ is the Boltzmann's constant, and W is the number of microstates}$$

Or, in more modern notation:

$$S = k\ln(\Omega)$$

Where k is the Boltzmann's constant, ln is the natural logarithm, and omega, Ω, is the number of microstates. In the past, log was just another way to write the natural logarithm. Also, omega is now used to avoid confusion, because W is used to represent too many things. Note how the natural logarithm of 1 is zero, because there is no entropy when the molecules can only be in a

Chapter 5: Thermodynamics

single arrangement. Also, note that 1 is the minimum number of microstates, because the natural logarithm gives either an undefined or impossible negative value for any number less than 1.
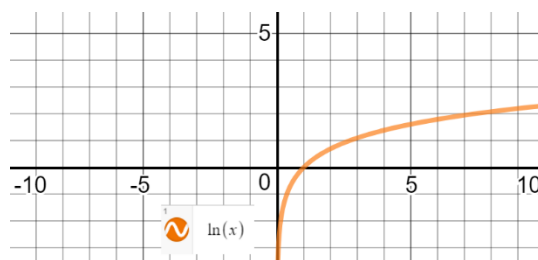

Figure 5.10. A graph of y=ln(x).

Interpretation of the Boltzmann Entropy Formula

You can see that if you arrange any large number of molecules, your number of microstates, or how many ways the molecules can be arranged, is going to be huge, especially when you are dealing on a scale of moles of things. Thus, entropy is very big, unless if you happen to be at absolute zero, and the molecules are all arranged in a perfect crystal lattice which allows only one arrangement that the molecules, thus leading to the Ω equaling one and the logarithm being zero, and therefore, has zero entropy. Also, because of the fundamental postulate of statistical mechanics, every microstate is equally likely to be occupied. Because neither being in a perfect crystal nor being at absolute zero is possible, which makes occupation of many microstates possible, entropy, and lots of it, will always be present. Thus, entropy is the degree of freedom the system has when arranging itself in various microstates. When all of the probabilities are summed, then they add up to the behavior of the entire system, which is called the macrostate. The Boltzmann entropy formula was later modified and built upon by many people, with famous examples being the Gibbs entropy, Shannon entropy, and the von Neumann entropy. The Boltzmann entropy formula is consistent with the classical heat engine entropy, as described by the Clausius inequality $dS \geq \frac{dq}{T}$, and predicts the irreversibility of every possible process.

Consequences of the Second Law

Heat Death of the Universe

The second law suggests that eventually, all energy in the universe will be so randomly dispersed, that everything would be nearly stochastically the same. That means that there will be no colder nor hotter portions of the universe, and everything would be at the same temperature. Since Carnot and Clausius pointed out that for heat to do useful work, it must go from a hotter heat source to a colder heat sink, when the universe becomes uniform, no more work is possible. This is known as the possible heat death of the universe. Most of the universe is estimated to be at an average of 2.73 K. However, we are not getting there anytime soon, because the expansion of the universe increases the possible maximum entropy of the universe, meaning that the universe is capable of performing more processes before it reaches homogeneity. This is known as the entropy gap, that allows the universe to keep on functioning and sustaining life.

Time's Arrow

Since entropy always increases, and time only increases, there is speculation that the passage of time, or time's arrow, has to do with increases in entropy. For example, if you watched a video of somebody catching a ball in reverse, the ball would appear to be thrown rather naturally. Thus, throwing and catching balls is rather time symmetric, in that the same type of motion occurs whether it is observed forwards or backwards in time. However, entropy increases when time moves forward, as mechanical energy is lost. Without dissipation of energy, then there would be nothing that differentiates throwing a ball, and catching a ball. Both would be energetically possible, for an infinite number of times. Thus, since things cannot go on infinitely, and time passes irreversibly forwards, we have good reason to think that there is an irreversible quantity that governs our universe, that increases whenever anything occurs.

Chapter 5: Thermodynamics

Figure 5.11. A stroboscopic photograph of a basketball bouncing. Note how we can see that it loses energy as it bounces, as it does not return to the same height.

Impossibility of Processes Allowed by the First Law

Yet, another way to approach entropy is to observe processes that obey the first law of thermodynamics. An adiabatic process is a process that does not allow heat to enter nor escape the system. It is a type of ideal process, which is useful for discussing ideal situations. It was found that from a state, very often you can go to another state by only adiabatic processes. However, once you go to the second state, it was found that you cannot go back to the first. This is an issue of irreversibility, in that the process, although it conserves energy, cannot return itself back to where it started. This problem of adiabatic inaccessibility is another example of entropy, because entropy is the source of irreversibility. Although reversing the process is energetically possible, in that the system has enough energy to do so, it is simply not physically possible because the energy is no longer orderly enough to return to the original state. This adiabatic accessibility definition of entropy was first pioneered by Constantin Carathéodory, in his "Investigations on the Foundations of Thermodynamics," and later formalized by Elliot H. Lieb and Jakob Yngvason in 1999. Thus, this is a rather modern theory of entropy, and is commonly illustrated in various texts.

Chapter 5: Thermodynamics

The Third Law of Thermodynamics

The Nernst, Lewis-Randall, and Nernst-Simon Statements

Following the first three laws (the zeroth, the first, and the second laws of thermodynamics), the third law of thermodynamics was formulated. In 1912, Walther Nernst stated that it is impossible to reach absolute zero. In 1923, Gilbert N. Lewis and Merle Randall stated that the entropy of a perfect crystal is equal to zero at absolute zero. It makes sense, because there is no uncertainty in where the molecules are when they are locked into a perfect lattice and are not moving. Thus, with the statistical mechanics entropy formula, the number of possible microstates, Ω, is equal to 1, the natural logarithm of 1 is equal to 0, and the calculated entropy is zero. When the molecules are above 0 K, or not in a pure perfect crystal, there is much possibility for disorder. Because both perfect crystals and reaching absolute zero are impossible, everything has positive entropy. An equivalent consequence of the third law of thermodynamics is the Nernst-Simon statement, that the entropy of a reversible isothermal process is zero at absolute zero. Francis Simon was Nernst's student. Since we need to perform a reversible process at absolute zero to get 100% efficiency, and reaching absolute zero and performing reversible processes are both impossible, we cannot ever get 100% efficiency.

Energy

Forms of Energy

Energy comes in many forms. Some energy is stored for future use. For example, if I put a brick on my roof, I just gave it gravitational potential energy. Thus, it has the potential to convert that potential energy to kinetic energy, if it falls. When it hits me on the head on the way down, it gives the kinetic energy to me, some of which is converted to thermal energy during the collision. I probably will not feel very energetic, even with this decently large amount of energy added to my brain.

Let us find how we can calculate the gravitational potential energy, kinetic energy, and velocity of the brick. Since gravity is fairly consistent if we stay close to the surface of the earth, potential energy, U_g, is pretty much equal to mgh, where m is the mass in kilograms, g is the acceleration due to gravity at the earth's surface, and h is the height of the roof the brick is on, relative to the ground. The mass of the brick is in kilograms, acceleration due to gravity is in

Chapter 5: Thermodynamics

meters per second squared, and the height is in meters. When we multiply kilograms by meters per second squared, and then multiply by meters, we get kilograms times meters squared divided by seconds squared. We arrive at the correct base unit expression for our SI derived unit of energy, the joule. For objects with mass equal to or greater than the molecular scale, and are not travelling anywhere near the speed of light, kinetic energy, K, is roughly equal to ½ mv^2. Thus, when the brick falls, if it does not lose energy to air resistance, whatever mgh it expends becomes K, and the brick now has a velocity, v, of $\sqrt{\frac{2K}{m}}$. According to the conservation of energy, if gravitational potential energy is all converted into kinetic energy, $U_g = mgh$ is equal to $K = \frac{1}{2}mv^2$. If we substitute in K for the mgh, we get $v = \sqrt{\frac{2mgh}{m}} = \sqrt{2gh}$.

Dissipation of Energy

Whenever useful mechanical energy becomes dissipated, it is usually lost as heat, q. This conversion is usually generated by dissipative forces, such as friction or drag. This leads us to the next principle, that moving against the influence of a force decreases the kinetic energy of an object, and moving in the same direction of a force increases the kinetic energy of an object. So, since the falling object moves in the same direction that the force of gravity pulls it, the velocity of the object increases as it falls.

Conservative vs. Nonconservative Forces, and the Conservation of Mechanical Energy

Some forces are conservative, and others are not. By conservative, we mean that the force conserves the mechanical energy of the object it acts upon. Mechanical energy is the sum of potential and kinetic energy. Although mechanical energy can be lost, total energy is always conserved, according to the first law. If I move the object against the force of gravity, which is a conservative force, I give it gravitational potential energy. However, with dissipative forces such as friction, the energy converted to heat due to friction cannot be given back to the object that lost the mechanical energy, because friction always opposes the direction of motion.
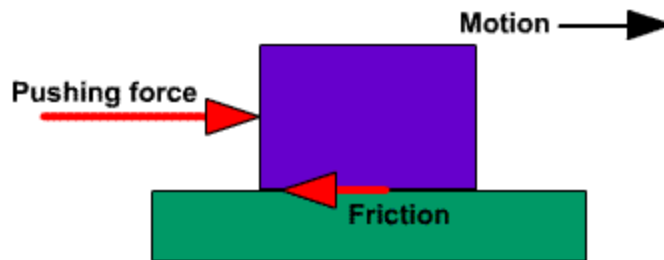
Chapter 5: Thermodynamics

Figure 5.12. Friction always opposes the direction of motion. Therefore, it leads to dissipation of energy, and an applied force is necessary to keep the block moving.

Therefore, friction will always slow an object down. Notice that forces that do not change direction when you change the direction of the object can possibly give the energy back, whereas forces that change direction when you change the direction of the object cannot give the energy back. However, in real processes, mechanical energy is always dissipated. This follows from the second law of thermodynamics, because dissipation make it impossible to do anything without wasting a portion of the energy invested.

Transfer of Energy

Just like there are many forms of energy and many ways to convert energy into its various forms, there are also many ways to transfer energy from one object to another, or one system to another. For example, when we throw a ball, we do work on the ball by giving it kinetic energy. Some of the work we do propels the ball in the opposite direction that gravity pulls, because we usually throw balls at an upward angle. As long as the ball is in the air, it has gravitational potential energy. When the ball falls towards the ground, the force of gravity converts the available gravitational potential energy to kinetic energy. You may say, why does the ball eventually cease to bounce? Although some energy was returned as elastic potential energy every time the ball bounces, a portion of its kinetic energy is converted to thermal energy when the ball hits the ground, and also sound energy that you hear. When all the kinetic energy has become dissipated, the ball can no longer bounce. Thus, macroscopic mechanical work often transfers energy. Likewise, when a gas expands and pushes the atmosphere, the gas does some work.

Chapter 5: Thermodynamics

However, not all transfers of energy are macroscopic. For example, when we turn on a light bulb, we do not see the electrons moving. When the electrons emit their energy as photons, you see the collective effect of numerous photons as light, but you cannot single out the individual photons that were emitted. When heat is transferred, very often the transfer is microscopic. Heat transfer by convection can sometimes be observed as a macroscopic effect when the medium is seen moving. However, conduction and radiation are not seen for the most part. Heat is usually described as the kinetic energy of the molecules, and you cannot see those molecules. When the molecules collide, they transfer kinetic energy to each other, and conduction occurs. When the molecules give off heat energy as radiation, it can travel through space as photons, and it can be absorbed. However, unless if the radiation is in the visible spectrum, you cannot see it, forget about seeing all the individual photons. Kinetic energy as heat is usually random, and generally is the result of the loss of energy that could have done useful work. The difference between macroscopic kinetic energy of an object and microscopic kinetic energy of a collection of molecules is that most of the kinetic energy of a macroscopic object can be quite easily converted to other forms of energy and used for useful work, whereas heat energy, the kinetic energy of microscopic particles, cannot be easily channeled into something macroscopically useful. Thus, energy is often dissipated to many different particles, and it is very hard to direct the energy from all those small particles to do something useful.

State Functions

A state is a set of conditions that describes a system fully. A state function depends only on the current conditions of the system. State functions have no respect for history, and you cannot tell how the system got to the given state if you only know its current conditions. Something similar to a state function would be your location. By looking at you, I have no idea where you came from, and how you got here. There are many state functions that can be assigned to a system, and their values for a given state are always the same, and do not vary based upon how the system came to the current state. Therefore, they are useful for calculations, because we can assign them a fixed value for every state without having to account for what happened between the states that we are interested in. Two common examples of state functions are enthalpy and internal energy. Anything that has to do with how we change from one state to

Chapter 5: Thermodynamics

another is not a state function, because state functions do not involve the process of change. State functions only depend on state, and do not vary depending on history. For a state function, if we know the final and initial states, we know exactly how much change occurred. For example, pressure, volume, temperature, and number of moles are state functions, as they only depend upon the state of the system. However, for quantities that are not state functions, we cannot easily know how much change occurred in these quantities without knowing the exact path taken to get from one state to the next. For example, the amounts of heat and work it takes to result in a given change in energy depends upon how we bring about that energy change. Thus, heat and work are not state functions, because they can vary depending on how you get from one state to another.

Measurement of Energy

Symbols:

Now, we have some more mathematical descriptions, so that we can quantitatively describe what occurs during processes that require thermodynamic analysis. This involves introducing some symbols to represent what we just discussed earlier. E is the general symbol for energy, and can be used for any form of energy. However, distinguishing one form of energy from another is important, which is why there are other symbols that represent distinct forms of energy. In a classical thermodynamic system, there are generally three types of energy. Potential energy, U, is energy that can be converted to some other form of energy. For an object, it is the energy of being positioned in a place where there is some force that can act on the object. We put a subscript on the U to indicate what type of force that can act on the object to give the object potential energy. We also use U for the internal energy of a system. Chemical potential energy is simply electrostatic potential energy on the molecular scale. In the special case of chemical potential energy, the energy that is released when the reaction proceeds originate from the difference in the electrostatic potential energy of the reactant and product molecules. Kinetic energy, the energy of motion, is another major form of energy. It is most often represented by the symbol K, or the symbol E_K. The third common form of energy, thermal energy, is kinetic energy on the microscopic scale. We also call thermal energy heat, and amounts of heat that are

Chapter 5: Thermodynamics

transferred is represented by the symbol q. Energy that is transferred in an orderly fashion by applying a force over a certain distance is called work, w.

Reference States

Energy is very difficult to measure, because we sometimes cannot directly sense energy. Even if we can sense it, we have different experiences depending on the type of energy at hand. It is even more difficult when we are trying to define the amount of energy that something on the molecular scale has. However, over the past century, we created a standardized way to measure changes in energy by establishing a reference point, called a standard state, and then deriving all other thermodynamic quantities with respect to that reference point. Since most reactions are carried out at about room temperature, the standard state is most commonly defined to be at a pressure of 1 atm (which is approximately 1 bar), and a temperature of 298.15 K. Therefore, when reactions occur, we can tabulate how much change in energy has occurred by comparing the energies of the reactants and products. Since most reactions occur in open air, where the pressure is relatively constant, the most commonly used thermodynamic quantity is enthalpy, which measures the amount of heat released or absorbed at constant pressure.

Change in enthalpy is roughly equal to change in energy, as long as large changes in volume, such as changes in amount gas, is not involved. We define the standard enthalpy at SATP of the pure elements to be equal to $0 \frac{J}{mol}$, which simplifies calculations by allowing us to neglect pure elements at standard state from our equations. For compounds, we define their standard enthalpy of formation to be the amount of heat gained or released when one mole of the compound is formed from its pure elements at standard temperature and pressure. These quantities are recorded in molar form, because the change due to a single molecule is relatively insignificant. However, because they are recorded in molar form, standard enthalpies of formation are tabulated in kilojoules per mole, as Avogadro's number is quite large. Note that most stable compounds have a negative standard enthalpy of formation, because the release of heat forms stable bonds, which may then only be broken by the addition of the same amount of heat that was released.

Chapter 5: Thermodynamics

Internal Energy

Changes in Internal Energy:

Like enthalpy, internal energy is difficult to measure directly. However, also like enthalpy, changes in internal energy is relative to a standard zero. The internal energy of the system changes when work or heat is added to or removed from the system, and change in the internal energy is equal to the change in heat and work added together.

$$\Delta U = q + w, \text{ where } q \text{ is heat, and } w \text{ is work}$$

Heat and work have signs. An influx of heat corresponds to a positive q, and a loss of heat corresponds to a negative q. Likewise, work done on the system has a positive w, and work done by the system, has a negative w. Positive q and w result in energy being added to the system, and negative q and w result in energy being taken away from the system, which we usually define to be the atoms and molecules we are interested in.

pV work

In most chemical reactions, there is only pV work, meaning that all the work is the result of changes in volume in the presence of a pressure. Other forms of work include electrical work, and changing the velocity of the entire system. If we look at pV work from the standpoint of a massless piston, we use the external pressure, because the pressure that is actually pushing on the piston from the inside is the internal pressure of the region directly next to the piston. When the conditions of the system change, such as when the system is reacting, the pressure inside our system may not be the same throughout the entire system. That makes measuring the internal pressure that pushes the piston very difficult to do, because if we do not measure the internal pressure directly next to the piston, we can arrive at an incorrect result when we calculate our work done. However, the effective internal pressure on the piston is equal to the external pressure, as a result of Newton's second law. When reactions occur in open air, they occur at a pressure of about 1 atmosphere, which is approximately 101,325 pascals.

When work is done by expansion and compression, it is said to be pV work, because the work is due to a change in volume at a certain pressure. When there is only pV work, we have the following:

Chapter 5: Thermodynamics

$$w = -p_{ext}\Delta V, \text{where there is only } pV \text{ work, and } p_{ext} \text{is a constant}$$

Thus, in the special case of only pV work, and constant external pressure, we can rewrite our change in internal energy as follows:

$$\Delta U = q - p_{ext}\Delta V$$

Expansion, which increases volume, leads to negative values of w. This is because our system loses energy as it pushes out against the external pressure to do work on the surroundings. In the opposite case, compression, which decreases volume, the surroundings do work on the system which leads to positive values of w. Likewise, when a reaction involves formation of a gas, expansion leads to negative w, and when a reaction consumes gas, the reduction in volume leads to positive w. Thus, we see that who does the work and who the work is done on determines the sign of w. In our case, work done on our system is always positive, and work done by our system is always negative.

Transfer of Energy by Heat

Change in the amount of heat is also measured in joules, because heat is another way to measure energy added to or taken from a system. In a reaction, temperature differences govern whether heat will be absorbed or released from the system. Remember that we are only interested in the reactants and the products, so we define our system to consist of only the atoms and molecules. When the temperature of the system is lower than that of the surroundings, heat is given to the system, and q is positive. However, if the temperature of the system is higher than the temperature of the surroundings, heat is given off by the system to the surroundings, and q is negative. In an exothermic reaction, you feel the warmth because of the heat released when the reactants become the products. The released heat dissipates to the surroundings, which you are a part of. The opposite applies for an exothermic reaction, where heat is absorbed from the surroundings as the reactants become the products. Remember that our system consists of solely the reactants and products. When reactions are carried out in solution, the solvent molecules that do not participate in the reaction are not considered part of our system. Our reaction occurs and transfers heat with the immediate surroundings, which is the rest of the solution. Then, the solution then tries to gain or lose heat to become at the same temperature with its surroundings,

Chapter 5: Thermodynamics

which is the rest of the universe. Thus, when exothermic reactions are carried out in solution, the temperature of the solution increases, and when endothermic reactions are carried out in solution, the temperature of the solution decreases. During endothermic reactions and processes, q is positive, because our system is absorbing heat. During exothermic reactions and processes, q is negative, because our system is releasing heat.

Changes in Internal Energy, When Volume is Held Constant

When volume is held constant, such as in a bomb calorimeter, there is no pV work. Thus, if there are no other forms of work, the change in internal energy has to occur solely through transfer of heat. This offers us a very easy way to measure the change in internal energy for a reaction, which is bomb calorimetry. Bomb calorimetry relies on measuring temperature changes when we conduct the reaction while keeping the volume constant. The volume is kept constant by the rigid container called a bomb cell.
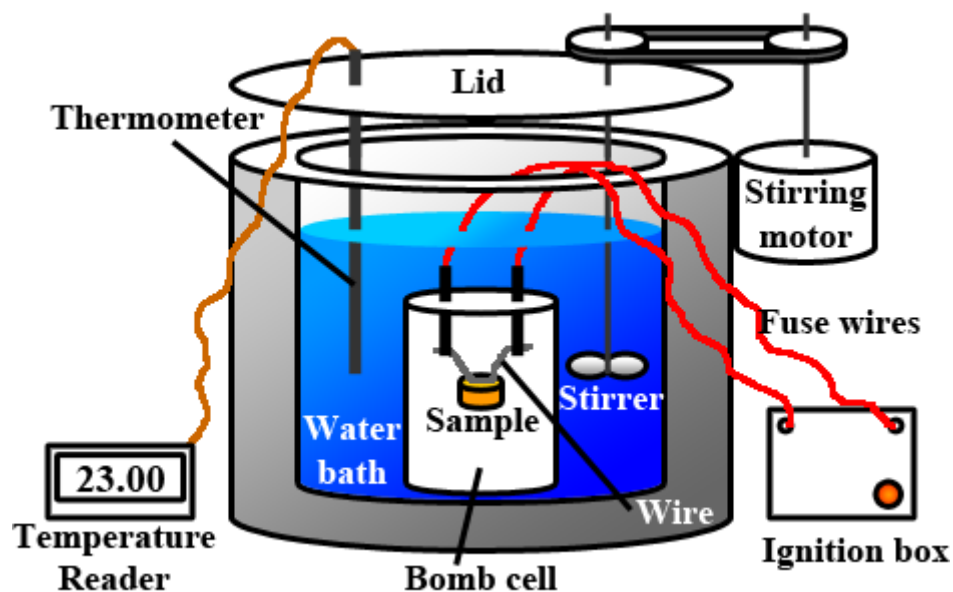

Figure 5.13. A diagram of a constant volume bomb calorimeter, used for measuring changes in internal energy.

For a given change in temperature, the kinetic energy of the molecules is increased by a certain amount. Thus, we defined a value, that at a given temperature for a system, relates the

Chapter 5: Thermodynamics

amount of energy transferred to the change in temperature. This is called the heat capacity of the system, or C. C is equal to the amount of heat transferred, divided by the change in temperature. However, C varies based upon the conditions present. For example, very often, we define a heat capacity of a substance based upon a mole of that substance. That is called the molar heat capacity, C_m. Other times, we define a specific heat capacity, c, which is equal to the amount of heat that it takes to raise the temperature of one gram of the substance by one kelvin. Also, heat capacity varies based upon pressure and volume conditions. Thus, in the case of bomb calorimetry, where volume is constant, we are especially interested in C_V, which is the constant volume heat capacity. The subscripted $_V$ indicates constant volume conditions.

To calibrate the bomb calorimeter before use, a known amount of a standard substance is burned. Most commonly, the substance used is benzoic acid. Since we already know the amount of heat released from burning the known amount of standard substance, we can calculate the constant volume heat capacity for the bomb calorimeter. If there is a large variation in temperature, we need a calibration curve, which gives us the constant volume heat capacity of the calorimeter over a range of temperatures. However, if the temperature change is small, the heat capacity does not significantly change, and we can apply the following approximation:

$$\Delta U \approx C_V \Delta T$$

This can also be written in terms of the specific heat capacity at constant volume:

$$\Delta U \approx m c_V \Delta T, \text{ where } c \text{ is the specific heat, and } m \text{ is in grams}$$

Note that these equations are only valid when the volume is kept constant, because the heat capacity depends on the conditions of the system. The rigid walls do not allow compression nor expansion, which permits us to make the approximation. Since most reactions occur over a relatively small temperature range, we apply the equation above very frequently. However, if the temperature range is large, we would need a constant volume heat capacity graph for the bomb calorimeter, or more preferably, reduce the amount of reactant that we use.

$$\Delta U \approx m c_V \Delta T \approx C_V \Delta T$$

Chapter 5: Thermodynamics

Enthalpy

Since most reactions occur in open air, we defined another thermodynamic state function called enthalpy, represented by H. Open air is at atmospheric pressure, which is fairly constant, and enthalpy is designed so that it is convenient at constant pressure. Enthalpy, and changes in enthalpy, are defined as follows:

$$H = U + pV$$

Again, when we deal with change, we find it easier to use the external pressure.

$$\Delta H = \Delta U + \Delta(p_{ext}V)$$

When the pressure is constant and only pV work occurs, we result in the following:

$$\Delta H = \Delta U + p_{ext}(\Delta V) = q + w + p_{ext}\Delta V = q - p_{ext}\Delta V + p_{ext}\Delta V = q$$

Thus, constant pressure calorimetry is effective when there are no gases involved. If there are gases, it is difficult to keep track of all the reactants and products, and the error of the technique sharply increases. In the case when no gases are involved, pV work is usually pretty close to zero, making the change in enthalpy very close to the change in internal energy. In the case where the reaction is occurring in open air, and there is no work, we find the following. This is approximately true for most solids and liquids over small temperature ranges:

$$\Delta H = q \approx \Delta U$$

Change in Enthalpy at Constant Pressure

The change in enthalpy of a reaction can also be found in a similar way, as it was found when we were working with the change in internal energy. This time, we use constant pressure calorimetry, which is the familiar Styrofoam coffee cup calorimetry. Given that there are no gases involved, there is nearly no change in volume. Thus, change in pV is approximately zero. Again, we can also make a similar approximation as we had done before for the constant volume calorimetry. Thus, at constant pressure over small temperature ranges, we can write the following, where the subscripted p indicates constant pressure conditions:

$$\Delta H \approx C_p \Delta T \approx mc_p \Delta T$$

Chapter 5: Thermodynamics

Notice that here, the heat capacities are all for constant pressure.

Figure 5.14. A picture of a Styrofoam coffee cup constant pressure calorimeter, used primarily for determining changes of enthalpy.

An Approximate Conversion Between Change in Enthalpy and Change in Internal Energy for Ideal Gases

Remember when we said that change in internal energy and change in enthalpy are approximately equal if there are no gases involved? That is because it is very difficult to evaluate $\Delta(pV)$ for nonideal gases. However, in the case of ideal gases, conversion between internal energy and enthalpy is very easy if we know the amount of gas generated, because we have the ideal gas equation.

$$\Delta H = \Delta U + \Delta(pV)$$

Now, from the ideal gas equation, we substitute in:

$$\Delta(pV) = \Delta(nRT), \text{ideal gases only}$$

$$\Delta H = \Delta U + \Delta(nRT), \text{ideal gases only}$$

Now, you may wonder, how does replacing a term with two variables with a term with two variables and a constant make the calculation easier? It turns out that the conversion can only be applied easily when the temperature is held constant. Thus, if the reaction occurs at constant temperature, we are effectively replacing a term with two variables with a term that

Chapter 5: Thermodynamics

contains two known constants and a single variable. So, at constant temperature, the conversion becomes:

$$\Delta H = \Delta U + (\Delta n)RT, \text{constant } T, \text{ideal gases only.}$$

$$\Delta n \text{ is the change in number of moles of GAS}$$

And, at constant pressure,

$$q = \Delta U + (\Delta n)RT, \text{constant } T, \text{ideal gases only.} \Delta n \text{ is the change in number of moles of gas}$$

$$\Delta U = q - (\Delta n)RT, \text{constant } T, \text{ideal gases only.} \Delta n \text{ is the change in number of moles of gas}$$

Likewise:

$$\Delta U = \Delta H - (\Delta n)RT, \text{constant } T, \text{ideal gases only.} \Delta n \text{ is the change in number of moles of gas}$$

And, at constant volume,

$$q = \Delta H - (\Delta n)RT,$$

$$\text{constant } T, \text{ideal gases only.} \Delta n \text{ is the change in number of moles of gas}$$

$$\Delta H = q + (\Delta n)RT,$$

$$\text{constant } T, \text{ideal gases only.} \Delta n \text{ is the change in number of moles of gas}$$

Thus, the relation above may be readily applied in near ideal equations to approximately convert between the two, if we assume ideal gas behavior. Note that Δn is the change in number of moles of gas, as solids and liquids do not have significant expansion. Thus, we see that when we do not have gases involved, we do not have a significant $\Delta(pV)$, thus our ΔH would then be approximately equal to ΔU.

Ideal Gases, and Basic Consequences of Statistical Mechanics

According to the kinetic molecular theory, which statistical mechanics is founded upon, the kinetic energy of the molecules is responsible for heat. Although in some ways it is restricted due to its assumptions, it does offer a fairly good model to base microscopic theories on. Since I do not have the space to explain it sufficiently, I'll give you a few quick principles. The first, is that every system at a given state has many levels of energy that are available to the molecules in

Chapter 5: Thermodynamics

the system. This is due to the Maxwell-Boltzmann distribution, which describes the probability of a particle having a certain speed, thus a certain amount of kinetic energy. The higher the temperature, the more energy, and the faster the gas molecules move. At low temperatures, the Maxwell Boltzmann distribution predicts that most of the molecules will be at relatively low speeds. Thus, there is a high peak. At higher temperatures, some of the molecules have larger amounts of energy, and the peak decreases in height, and the distribution spreads over a larger range of speeds, but overall the molecules have more thermal kinetic energy. Thus, more energy levels are available as the temperature increases, in accordance to Boltzmann, that increasing energy allows for the particles to occupy more states that become energetically available when temperature increases. The Maxwell Boltzmann distribution does not vary with the mass of the particles, as it deals with energy, which accounts for the mass.
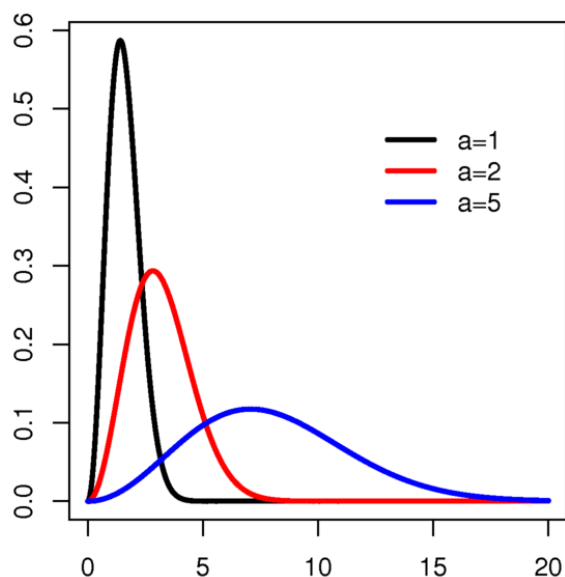

Figure 5.15. A Maxwell-Boltzmann distribution graph for three different temperatures. The probability is on the y axis, and the temperature is on the x axis. The area underneath each probability distribution is equal to 1, because a particle must have a velocity. Notice how when temperature increases, the peak decreases in height, and the distribution is more spread out.

The second is that although the different gas molecules move at different velocities, when we sum up the energy of the system, the energy is constant for the system as long as the temperature is constant. This is one reason why statistical mechanics is called statistical, because

Chapter 5: Thermodynamics

we do not know the individual motions of the molecules. Rather, we take the sum of the properties of all the molecules, which is statistically constant, or stochastic.

Equipartition

Based on the previous principle, each molecule, on average, has a certain amount of kinetic energy due to translational, rotational, and vibrational motion. This is called the equipartition principle.

For Translational Kinetic Energy:
For translational motion, the following is the relation between velocity and kinetic energy, where the total translational kinetic energy is equal to the sum of the translational kinetic energy in the x, y, and z directions:

$$K_{translational} = \frac{1}{2}mv^2 = \frac{1}{2}m(v_x)^2 + \frac{1}{2}m(v_y)^2 + \frac{1}{2}m(v_z)^2 = \frac{1}{2}m((v_x)^2 + (v_y)^2 + (v_z)^2)$$

We can check that the last expression equals the initial expression, because of the 3-D analogue of the Pythagorean theorem:

$A^2 + B^2 + C^2 = D^2,$

where A, B, and C are along the cartesian axes at right angles to each other, and D is the distance from the origin (0,0,0) to the point (x, y, z).
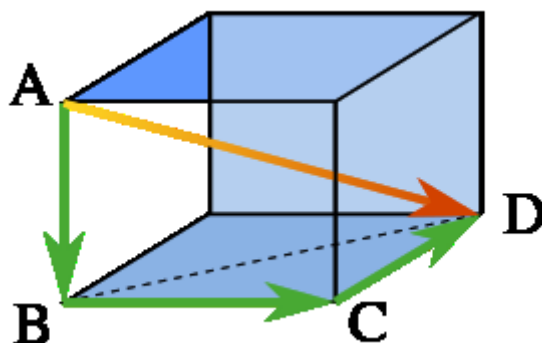

Figure 5.16. The 3D Pythagorean theorem may be applied to find the distance from A to D, if the distances AB, BC, and CD are known.

Chapter 5: Thermodynamics

For an ideal gas, the temperature is proportional to the kinetic energy. Thus, if the mass of the particle is kept constant, the square of the velocity is proportional to the temperature.

$T \propto K$, and $K \propto v^2$, therefore $v^2 = wT$, where w is some constant of proportionality

Going back to our equation for energy, we have:

$$K = \frac{1}{2}mv^2 = \frac{1}{2}mwT$$

This is where we do the equipartition. We separate the translational kinetic energy to the kinetic energy due to translation in the x, y, and z directions, and since the motion of the large number of particles is random, we assign the same amount of energy to translational motion in each of the three directions.

$$K_{translational} = \frac{1}{2}mv^2 = \frac{1}{2}m(v_x)^2 + \frac{1}{2}m(v_y)^2 + \frac{1}{2}m(v_z)^2 = \frac{\frac{1}{2}mwT}{3} + \frac{\frac{1}{2}mwT}{3} + \frac{\frac{1}{2}mwT}{3}$$

Then, since mass is a constant, we combine the mass with the constant w, and the constant 1/3, to make a new constant, which we will call k. This k is very important, and it is the same k that we saw previously as the Boltzmann constant in the ideal gas equation, and the Boltzmann entropy formula.

$$K_{translational} = K_x + K_y + K_z = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT$$

Thus, we just divided up the translational kinetic energy of the molecules into the three spatial directions evenly, and related the kinetic energy to temperature.

For Rotational Kinetic Energy:
Likewise, for rotational kinetic energy, which is significant for gases that are not monatomic, we have the following:

$$K_{rotational} = \frac{1}{2}I\omega^2, \text{where } I \text{ is the moment of inertia, and } \omega \text{ is the angular velocity}$$

Chapter 5: Thermodynamics

Here, the moment of inertia is a measure of resistance to rotational acceleration by torques, much like how mass is a measure of resistance to linear acceleration by forces. Therefore, we do nearly the same exact procedure, of separating the rotational kinetic energy into rotation in the xy plane, rotation in the yz plane, and rotation in the xz plane. If we relate temperature to the energy of rotation, we arrive at the same result, that for every rotational degree of freedom, the molecule has an additional $\frac{1}{2}kT$ of energy. Note that for monatomic gases, we do not count the rotation around a nucleus, thus leaving zero rotational degrees of freedom, and for diatomic gases and linear gases, we do not count rotation around the bond axis, thus leaving two degrees of freedom. This is because the radii of the nuclei are too small for its rotational energy to be significant.
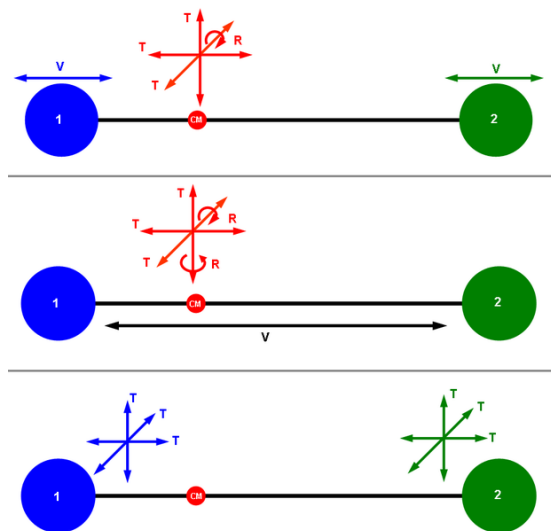

Figure 5.17. A diatomic molecule only has two modes of rotational motion, because rotation around the bond axis is insignificant.

Thus, to bring gases up to a certain temperature from absolute zero, you need $\frac{3}{2}kT$ per molecule of additional energy for polyatomic gases that are not linear, and kT per molecule of additional energy for linear gases, relative to monatomic gases. Vibrational degrees of freedom only are significant at very high temperatures. Thus, they are relatively unimportant, and we will not consider them here.

Chapter 5: Thermodynamics

Heat Capacities

Therefore, for a monatomic ideal gas, we have 3 translational degrees of freedom, in the x, y, and z directions. Since rotating a nucleus is relatively insignificant, we do not need to consider that. For a diatomic or linear ideal gas, we again have 3 translational degrees of freedom, and also 2 rotational degrees of freedom. Note that again, rotating around the bond axis of the molecule is insignificant in this case. For a polyatomic nonlinear molecule, we have 3 translational and 3 rotational degrees of freedom. Thus, monatomic ideal gas particles have an average of $\frac{3}{2}kT$, linear, $\frac{5}{2}kT$, and polyatomic nonlinear, $3kT$ joules of energy. This is important, because of two reasons. The first, is the heat capacities of monatomic, linear, and nonlinear polyatomic gases. Since heat capacity of ideal gases are constant, due to the lack of attractive and repulsive interactions, simple division allows us to find the heat capacities, which are just equal to q/T. Multiplying the average energies of the molecules by Avogadro's number gives us the energy of a mole of the gas at a given temperature. We recall that the molar gas constant is equal to the Boltzmann's constant multiplied by Avogadro's number. Thus, we find the molar kinetic energies are $\frac{3}{2}RT$, $\frac{5}{2}RT$, and $3RT$ respectively, and that the molar heat capacities at constant volume are equal to $\frac{3}{2}R$, $\frac{5}{2}R$, and $3R$ respectively. To find the molar heat capacities at constant pressure, we apply the relation we just talked about.

$$H = U + pV$$

$$q = U + pV, \text{at constant pressure}$$

$$q = U + nRT, \text{at constant pressure and for ideal gases only}$$

Rearranging, and substituting in the molar kinetic energies in for U (which are just ΔU from absolute zero to T), for 1 mole of gas we get:

$$q = \frac{3}{2}RT + RT = \frac{5}{2}RT \text{ for monatomic}$$

$$q = \frac{5}{2}RT + RT = \frac{7}{2}RT \text{ for linear}$$

$$q = 3RT + RT = 4RT \text{ for polyatomic nonlinear}$$

Chapter 5: Thermodynamics

Thus, rearranging to obtain the definition of heat capacity, $C_{p,m}$, which is equal to the amount of heat added divided by the change in temperature, we obtain our molar heat capacities. Note that n is equal to 1 in all these equations, and here we have T being equal to the change in temperature from absolute zero to the current thermodynamic absolute temperature. ($T = \Delta T$ from $T = 0$ to T). An ideal gas is special, in that its heat capacity is always a constant, because the heat capacity for most real gases vary. Also, ideal gases are special, in that the kinetic energy of the gas particles, thus the thermal energy of the gas, is directly proportional to their internal energy and enthalpy. Thus, we have the following:

$$C_{p,m} = \frac{q}{T} = \frac{5}{2}R \text{ for monatomic}$$

$$C_{p,m} = \frac{q}{T} = \frac{7}{2}R \text{ for linear}$$

$$C_{p,m} = \frac{q}{T} = 4RT \text{ for polyatomic nonlinear}$$

Note also, that according to the ideal gas law, we can also substitute out the RT for pV_m, which is convenient if we know the pressure and the volume of the sample of gas. However, temperature is still the simplest to use, as it is the easiest to measure.

Relation Between Heat Capacities

We observe that $C_{p,m}-C_{V,m}=R$. This is known as Mayer's relation, and works fairly well for real gases as well. It makes sense that C_p is greater than C_V, because a certain portion of the energy given to the ideal gas by heat is expended when the gas expands. When we use the ideal gas law, we find that the energy used in the expansion of 1 mole of ideal gas is equal to R for every degree that the gas is raised. Thus, statistical mechanics helps explain heat capacities, and is exact for ideal gases, but should not be used too extensively to estimate data for real gases. To determine values for real gases, experimentation is a better option.

Chapter 5: Thermodynamics

Root Mean Speed

The third, is that a higher portion of gas molecules are distributed at higher velocities at higher temperatures. This is in accordance to the Maxwell-Boltzmann distribution, which describes the fraction of gas molecules of a gas at a given temperature have a certain speed, thus a certain kinetic energy. Again, drawing from the equipartition theorem, we can find the root mean square translational speed of the molecules that we are interested in. Since each molecule has 3 translational degrees of freedom, each molecule has $\frac{3}{2}kT$ joules of translational kinetic energy. Thus, applying our translational kinetic energy formula, $K = \frac{1}{2}mv^2$, we get:

$$K_{\text{mean}} = \frac{3}{2}kT = \frac{1}{2}mv_{\text{rms}}^2$$

v_{rms} is the root mean square speed.

Rearranging and solving for v_{rms}, we get:

$$\frac{3kT}{m} = v_{\text{rms}}^2$$

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}}$$

Note that the small m on the bottom is the mass of the molecule in kilograms. However, sometimes it is easier to work with molar values, so we can multiply the top and bottom of the fraction by Avogadro's number:

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}\left(\frac{N_A}{N_A}\right)} = \sqrt{\frac{3RT}{M}}$$

Where R is the molar gas constant, $8.314\frac{\text{J}}{\text{K}*\text{mol}}$, and M is the molar mass of the gas particles in kilograms. Thus, we obtained our root mean square speed, for an ideal gas.

Chapter 5: Thermodynamics

Graham's Law of Effusion

From the previous relation between the root mean square speed, we can again verify Graham's law of effusion. We find that for an ideal gas, the velocity, which is proportional to the rate of effusion, is proportional to the square root of temperature, and is inversely proportional to the square root of the molar mass of the particles in kilograms.

Free Energy and Spontaneity

Entropy Again

We did a lot of discussion on the second law, and this quantity called entropy. But what physical significance does entropy have, that it is so important to sometimes calculate or measure it? It turns out, entropy governs whether reactions are spontaneous or not, along with the maximum amount of useful work we can get out of a process. For a given reaction, we have two types of common free energies. The first, is the Helmholtz free energy, and the other is the Gibbs free energy.

The Helmholtz Free Energy

The Helmholtz free energy, A, is defined as:

$$A = U - TS$$

Therefore,

$$\Delta A = \Delta U - \Delta(TS)$$

The meaning of free energy is energy that is available to do work. Therefore, if we know the possible change in Helmholtz free energy, we know the maximum amount of work that the system can do at constant temperature. The Helmholtz free energy is most useful when the temperature and volume is held constant, because of the change in internal energy term that becomes difficult to manage as pV work occurs. Thus,

$$\Delta A \leq \text{Maximum work that can be done by system}$$

$$\Delta A \leq w_{max}$$

Chapter 5: Thermodynamics

Note that the Helmholtz free energy is less than the work done by the system, because both are negative. They both represent a loss of energy. So, the change in Helmholtz free energy is a negative with a larger magnitude than the work we can make the system do. In cases of constant temperature, we can just do:

$$\Delta A = \Delta U - T(\Delta S)$$

And since the internal energy at constant volume is equal to the amount of heat transferred, at constant temperature and volume we can further simplify the calculation to:

$$\Delta A = q - T(\Delta S)$$

Apart from determining the maximum amount of work a system can do, we can also determine the theoretical spontaneity of a reaction at constant temperature and volume. When the change in Helmholtz free energy is negative, it means that the entropy of the universe is increasing for a reaction at constant temperature and volume, which is necessary for the reaction to proceed. Thus, the Helmholtz free energy provides a good rule of thumb.

$$\Delta A = \Delta U - \Delta(TS)$$

$$\Delta A = \Delta U - T\Delta S \text{ for constant temperature}$$

$$\Delta A = q - T\Delta S \text{ for constant temperature and volume}$$

$$-\frac{\Delta A}{T} = -\frac{q}{T} + \Delta S \text{ for constant temperature and volume}$$

Since the negative of q is the amount of heat transferred from the system to the surroundings, we see that $-\frac{q}{T}$, according to the Clausius inequality, is the entropy change of the surroundings due to heat given off or taken in by the system. We see, that on the right side, we have the entropy change of the system, $-\frac{q}{T}$, added to the entropy change of the system, ΔS, which is equal to the entropy change of the universe for the reaction. For a reaction to be spontaneous, the entropy change of the universe must be positive. Thus, we see that the associated change in Helmholtz free energy must be negative. Note that negative values of change in internal energy, and positive values in change in entropy tend to be favorable for a reaction to proceed. Any reaction that has a free energy less than zero is considered

Chapter 5: Thermodynamics

thermodynamically favorable, because the transfer of energy results in more entropy for the universe, which also confers more stability to the system.

The Gibbs Free Energy

The Gibbs free energy is defined as follows:

$$G = H - TS$$

$$\Delta G = \Delta H - \Delta(TS)$$

As expected, because change in enthalpy is involved, the Gibbs free energy is most useful when the temperature and pressure is held constant, because those conditions simplify calculations.

When temperature is held constant, we have:

$$\Delta G = \Delta H - T(\Delta S), \text{at constant temperature}$$

Adding the restriction of constant pressure, we have:

$$\Delta G = q - T(\Delta S), \text{at constant temperature and volume}$$

The Gibbs free energy is the maximum amount of nonexpansion work that a system can carry out at constant temperature. Thus, like the change in Helmholtz free energy, the change in Gibbs free energy is also related to work in the following fashion:

$$\Delta G \leq \text{Maximum possible non } pV \text{ work}$$

$$\Delta G \leq w_{\text{max,non } pV}$$

The Gibbs free energy is a metric of theoretical spontaneity of reactions that take place with temperature and pressure kept constant. Likewise, a decrease in Gibbs free energy also means that the system becomes closer to stability, and that the entropy of the universe is increased by transfer of energy. Note how here, the change in enthalpy plays the same role as the change in internal energy did for the Helmholtz free energy.

$$\Delta G = q - T\Delta S$$

$$-\frac{\Delta G}{T} = -\frac{q}{T} + \Delta S$$

Chapter 5: Thermodynamics

From this, we can see why most of the spontaneous reactions in everyday life (ex: fire) are exothermic. Exothermic reactions give heat to the environment, thus leading to a large increase in entropy. Thus, for a reaction to be spontaneous, we usually calculate the Gibbs free energy if the reaction occurs in open air, and the Helmholtz free energy if the reaction occurs in a constant-volume container. If the free energy is less than zero, then the reaction is considered thermodynamically favorable, and can proceed.

Chapter 5: Thermodynamics

Chapter 6: Thermodynamics Derivations

Exact and Inexact Differentials

An exact differential, is, as the name suggests, something that you know the exact change of, as you move from one state to another. The most common exact differentials are your state variables and state functions. Change involving state functions are exact differentials, because we know the exact difference that occurs when we change state. We use the small letter d to denote exact differentials. Quantities that we do not know the exact change in, as we move from one state to the next, are not state variables or state functions. These are your inexact differentials, which are represented by đ, or δ. The first is the more modern way to write it. The second is the traditional symbol. Therefore, changes in heat and work are inexact differentials, because we do not know exactly how much change in heat or work occur to obtain a given change in state.

Change in Internal Energy

Although internal energy is hard to measure, change in internal energy is measurable, and is defined to be comprised of a small amount of work, and a small amount of heat. Thus,

$$\mathrm{d}U = đq + đw$$

A d just stands for a very small Δ. Thus, it means a very small change in the value that follows the d. In words, the above statement means that a small change in internal energy is equal to a small change in heat and or work. When discussing internal energy, the above equation is what we will be using most frequently, because all our derivations must begin from the fundamental definition. Note that the small change in internal energy has the normal differential sign, whereas the small amounts of work and the heat have the stroked differential sign, đ. This indicates that work and heat are not state variables, and depend upon the path taken to arrive at the change in internal energy. Internal energy is a state function, and state functions do not depend on how you arrive at the quantity. The only thing that matters to a state function is the current condition of the system. Therefore, you know exactly how much change in the state function occurred. This means that we know the value of the exact differential, $\mathrm{d}U$, exactly.

Thus, a change in energy does not care if you obtained the change in energy all by heat, all by work, or by a combination of both. However, the amount of work and the amount of heat varies based upon how you obtain that change in internal energy. Therefore, given a change in state, the sum of the heat and the work always equals the change in internal energy, but the heat and work have different values depending on the processes that took place. Since the work and the heat are not state functions, they are inexact differentials, because we do not know the exact amount of work and heat that resulted in a given change in internal energy.

Definition of Work

Work is defined as the orderly nonthermal transfer of energy. Mechanical work is defined as the dot product of a force, and the distance that force moves an object. That means multiplying the component of a force in the direction of the object's motion, times the distance that the object is moved when the force is acting on the object.

$$đw = F \cdot dx = F\cos(\theta)dx = F\cos(\theta)dl, \text{ where } dl \text{ is the length the force acts on the object}$$
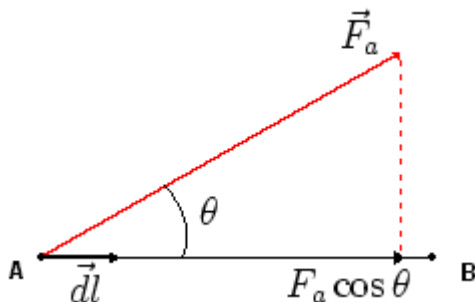
Figure 6.1. A diagram showing the distance that the force moves the object, dl, and the component of the force in the direction of motion, Fa*cos(theta).

The theta is just the angle between the force, and the direction the object is moving. However, most of the time in chemistry, the angle is either zero, or 180°, which means that the work is either the positive or negative product of the force and the distance the force pushes.

When θ equals 0 or 180°:

$$đw = F * dx \text{ for theta equals } 0°, \text{ and } -F * dx \text{ for theta equals } 180°$$

Chapter 6: Thermodynamics Derivations

Amount of energy transferred by work is measured in joules. It means that a small amount of work is equal to a force times a small change in distance. The reason why the stroked đ is used for the small change in work is because the amount of work done is path dependent. You can add 50 J to a system all by work, all by heat, or a combination of both.

Internal Pressure Equals External Pressure for a Massless Piston

Work due to expansion is usually analyzed from the perspective of a gas in a massless piston. For a massless piston, the forces on the piston due to the pressure inside and outside of the system are equal. This follows from Newton's second law, $F_{net}=ma$.

$$F_{net} = m_{piston}a = (0)a = 0, \text{ because the piston is massless}$$

Since the internal force is in the opposite direction of the external force, they have opposite signs. The net force is equal to the sum of all forces. The result obtained above suggests what is below:

$$F_{int} + F_{ext} = F_{net} = 0$$

$$F_{int} = -F_{ext}$$

Since pressure expressed in $\frac{kg}{m*s^2}$ is equal to force expressed in $kg\frac{m}{s^2}$ divided by area expressed in m^2, multiplying pressure by area yields force.

$$1 \text{ pascal} * m^2 = 1\left(\frac{kg}{m*s^2}\right)(m^2) = 1\frac{kgm}{s^2} = 1 \text{ newton}$$

Therefore, the following also holds.

$$|F_{int}| = p_{int}A = |F_{ext}| = p_{ext}A, \text{ where A is the area of the piston}$$

Note the absolute values. This is because pressure is always positive. This leads to:

$$p_{int} = p_{ext}$$

We have just proved that internal pressure on the piston is equal to external pressure on the piston.

Chapter 6: Thermodynamics Derivations

Change in Internal Energy, When There is Only pV Work

Notice that when we multiply the pressure by the area that the pressure is pushing on, we get the force. Then, when we multiply the force by a small distance, we get a small amount of work. Likewise, since multiplication is associative and commutative, when we multiply an area by a small distance, we get a small volume, and when we multiply that small volume by the pressure that is pushing, we get a small amount of work. Thus, when there is only expansion work, the following is true:

$$đw = -p * (\text{Surface Area})dx = -pdV, pV \text{ work only}$$
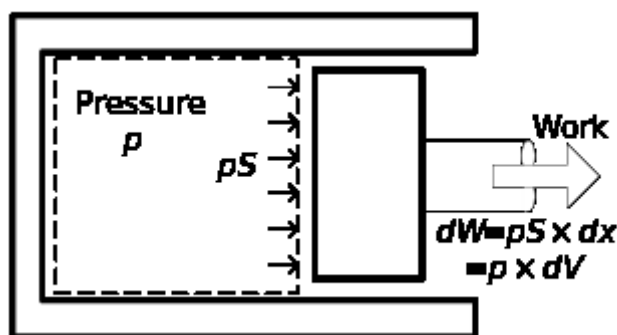
Figure 6.2. A diagram showing that the work done by the piston is equal to the pressure that the piston is moving against, multiplied by the surface area of the piston, multiplied by the distance the piston moves. Thus, work done by the gas in the piston is -pdV.

The work is negative, because our system is pushing the piston to expand a certain volume. Thus, in a system, a positive value for change in volume results in a negative value for energy due to work, because the system needs to use energy to push. When we push, we are pushing against an equal external force, as we have proved above. Therefore, we can write write:

$$đw_{pV} = -p_{ext}dV$$

In the case where there is only pV work, we can rewrite change in internal energy as:

$$dU = đq + đw = đq - p_{ext}dV, pV \text{ work only}$$

Chapter 6: Thermodynamics Derivations

The Sum of Very Small Differences Makes a Noticeable Difference

If the external pressure is rather constant, such as in the case of reactions occurring in open air, we use the external pressure to calculate work. To get the total amount of work done, w, we just add up the small amounts of work, đw. The big S, or $\int$, just means to add. Since it is placed before the small changes in work, đw, the following means to add up all the small amounts of work, to result in the total amount of work.

$$w = \int đw$$

Note that we do not use Δw, because work is already a quantity of change. However, we can write the change in internal energy due to work as:

$$\Delta U_{\text{due to work}} = \int_{State\ 1}^{State\ 2} đw$$

Where we get the total amount of work as equal to:

$$\Delta U_w = (\text{Total work done from } t = 0 \text{ to } t = 2) - (\text{Total work done from } t = 0 \text{ to } t = 1)$$

This means that subtracting work done at a given instant t=2, from work done at a later time, t=1, equals the change in internal energy due to work between the two times. Note that there is a reference time that has been provided, t=0. Although it is convenient to use t=0, any reference time may be used, so we can replace that t=0 with t=k, where k is any defined moment. However, we usually just write 1 and 2 instead of state 1 and state 2 above and below the $\int$, because of convenience. When doing thermodynamic calculations, you always need some form of a reference state. Since we are concerned with change, (thermo dynamics), it does not matter what we choose as a reference. What matters is if we have a reference, and can we easily use that reference to compare to our experimental values.

Change in Internal Energy, when External Pressure is Constant

If external pressure is constant, and only pV work is done, we can further simplify. This is usually the case, when reactions occur in open air. 1 atmosphere is approximately 101,325 pascals.

Chapter 6: Thermodynamics Derivations

$$w = -p_{\text{ext}}\Delta V, \text{where } p_{\text{ext}} \text{ is a constant, and only } pV \text{ work is done}$$

And

$$\Delta U = q - p_{ext}\Delta V, pV \text{ work only, constant external pressure}$$

Finding Changes in Internal Energy

We frequently use the following two equations:

$$dU = đq + đw$$

$$dU = đq - p_{\text{ext}}dV, pV \text{ work only}$$

Note that the volume is not an inexact differential, as volume is a state variable. If we know the conditions of the initial and final states, we can find the change in volume exactly. If we know the initial internal energy, we can find the final internal energy as follows. The equality $đw = -p_{\text{ext}}dV$ only hold when there is only pV work.

$$\Delta U = q + w$$

$$\Delta U = \int_1^2 dU = \int_1^2 đq + \int_1^2 đw = \int_1^2 đq + \int_1^2 -p_{\text{ext}}dV = \int_1^2 đq - \int_1^2 p_{\text{ext}}dV = q + w$$

$$pV \text{ work only}$$

Note that 1 and 2 to represents the states 1 and 2, not the integer values 1 and 2. However, in this case, we need to know the path taken from 1 to 2 if we want to find the integrals of the inexact differentials for work and heat. That is a royal pain, and we definitely do not want to be doing that, because are an infinite number of ways to get from state 1 to state 2. However, all those paths lead to the same change in internal energy. Therefore, we have a shorter way to calculate the change in internal energy, which is to use heat capacity and change in temperature.

The Partial Derivative and Heat Capacity

Now, for those of you who are unfamiliar with partial differentials, the concept is fairly simple. Partial differentials are just like normal differentials. They relate a tiny change in a variable to a tiny change in another variable, when other variables kept constant. Thus,

Chapter 6: Thermodynamics Derivations

$$\left(\frac{\partial U}{\partial T}\right)_{V,n}$$

just means the tiny change in U that is caused by a tiny change in T, with V and n kept constant. We can exclude the subscripts V and n, but we write them to remind us of the other quantities that can possibly vary. The partial differential shown above has a specific meaning. It is the heat capacity at constant volume, C_V. The subscript on the C indicates which variable is kept constant. Sometimes, it is easier to write the heat capacity in other forms, such as in molar form, $C_{V,m}$, or write it in per gram form, c_V. Note that we use lower case c for heat capacity per gram, as it has a special name, the specific heat. The following equivalent statements relate the change in internal energy versus the change in temperature and the heat capacities:

$$\left(\frac{\partial U}{\partial T}\right) = C_V$$

Where n is the number of moles of the substance:

$$\left(\frac{\partial U}{\partial T}\right) = nC_{V,m}$$

Where m is the mass of the substance in grams:

$$\left(\frac{\partial U}{\partial T}\right) = mc_V$$

Changes in Internal Energy, and the Constant Volume Heat Capacity

The heat capacity varies as a function of temperature. As a good rule of thumb, the law of Dulong and Petite states that for most crystalline solids, the molar heat capacity at constant volume is approximately $3R$. From the equipartition theorem, we have already seen the constant heat capacities of ideal gases. However, the approximation is often invalid, and your best bet in obtaining C_V values is by experimentally plotting a graph of C_V with respect to temperature. Multiplying a molar heat capacity at a given temperature by a small change in temperature results in a small amount of heat, which in turn, results in a small change in internal energy. Thus, we can rewrite the change in internal energy due to the change in temperature as follows:

Chapter 6: Thermodynamics Derivations

$$\dq = \left(\frac{\partial U}{\partial T}\right) \partial T = C_V \, dT$$

And for pV work only:

$$dU = \dq - p_{\text{ext}} dV, pV \text{ work only}$$

$$dU = C_V dT - p_{\text{ext}} dV, pV \text{ work only}$$

Then, integrating, we have:

$$\Delta U = \int_1^2 dU = \int_1^2 \dq + \int_1^2 \dw = \int_1^2 C_V dT - \int_1^2 p_{\text{ext}} dV, pV \text{ work only}$$

We get the same change in internal energy no matter what path we take from state 1 to state 2 because internal energy is a state function. However, the amount of heat and work vary, because the paths taken are different and the processes involved are different.

Whenever we see an integral with a variable that has another variable held constant, there is a path restriction. Since the heat capacity at constant volume is only valid when the volume is constant, whenever we change the temperature, we cannot change the volume. Likewise, whenever we change the volume, we cannot change the temperature. This forces the processes to follow straight, perpendicular lines to the axes on a T vs V graph if the external pressure is a constant. Thus, for us to evaluate the integral above, we need to choose a path where the volume is held constant whenever the temperature changes, and the temperature is held constant whenever the volume changes. We will see some of these path-dependent integrals later, and the conditions must be kept in mind whenever we evaluate them. One piece of advice is that whenever you see an integral involving something with a variable as a subscript (for example, C_V, C_p, etc.), then the variable subscripted needs to be held constant when there is any d-something (dT in this case), and the d-something must be zero when the subscripted variable changes, otherwise we cannot calculate the integral.

Chapter 6: Thermodynamics Derivations

Change in Internal Energy at Constant Volume, Along with Bomb Calorimeter Equations and Approximations

We have already seen our idealization of the work done when the external pressure is constant. Thus, substitution produces:

$$dU = đq + đw = đq - p_{ext}dV = C_V dT - p_{ext}dV, pV \text{ work only, and } p_{ext} \text{ is constant}$$

$$\Delta U = \int_1^2 dU = \int_1^2 đq - \int_1^2 p_{ext}dV = \int_1^2 C_V dT - p_{ext}\Delta V, pV \text{ work only, } p_{ext} \text{ is constant}$$

In an ideal situation where the volume is constant, and there is only pV work, which is equal to zero, we arrive at the following, which is even more ideal than the previous situation, where there is no work in general:

$$\Delta U = \int_1^2 dU = \int_1^2 C_V dT - \int_1^2 p_{ext}dV = \int_1^2 C_V dT - \int_1^2 p_{ext} * 0 = \int_1^2 C_V dT - 0$$

$$= \int_1^2 C_V dT, pV \text{ work only, } dV = 0, \text{ thus } p_{ext}dV = 0$$

Since the dV is included in the work term, if we make the dV=0 because volume is constant, then the work term drops out. Also, since we are using the constant volume heat capacity, this makes the calculation easy. For most cases, another approximation makes the calculation even simpler, and allows us to perform constant volume bomb calorimetry with ease. For a reaction at constant volume, if we assume that the constant volume heat capacity is roughly constant over small temperature intervals, we arrive at the following:

$$\Delta U \approx C_V \Delta T, \text{approximating that } C_V \text{ is roughly constant. } V \text{ is kept constant.}$$

This can also be written in terms of the specific heat capacity at constant volume:

$$\Delta U \approx mc_V \Delta T, \text{approximating that } c_V \text{ is roughly a constant. } V \text{ is kept constant.}$$

Thus, when volume is kept constant, and temperature change is fairly small,

$$\Delta U = \int_1^2 C_V dT \approx mc_V \Delta T \approx C_V \Delta T,$$

Approximating that heat capacity is roughly constant. V is kept constant.

Chapter 6: Thermodynamics Derivations

Change in Enthalpy

For constant pressure cases, it is often much easier to use another thermodynamic state function, enthalpy, which is denoted by H.

$$H = U + pV$$

$$dH = dU + d(pV)$$

$$\Delta H = \Delta U + \Delta(pV)$$

And, in the special case of an ideal gas, where $\Delta(pV) = \Delta(nRT)$, and with temperature held constant, we get:

$$\Delta H = \Delta U + (\Delta n)RT, \text{ for ideal gas only, and } \Delta n \text{ is the change in number of moles of GAS}$$

Using the following relation, we can also write the change in enthalpy when there is only pV work as follows, where pressure is not constant:

$$p_f V_f = (p_i + dp)(V_i + dV) = p_i V_i + V dp + p dV + dp dV$$

$$p_f V_f - p_i V_i = d(pV)$$

$$d(pV) = V dp + p dV + dp dV$$

Since $dp dV$ is the product of two infinitesimally small changes, it can be neglected. Thus, substituting in, we get:

$$dH = dU + d(p_{ext}V) = dU + p_{ext}dV + V dp_{ext} + dp_{ext}dV = dU + p_{ext}dV + V dp_{ext}$$

$$pV \text{ work only}$$

If there is no pV work, we can further write:

$$dH = dU + p_{ext}dV + V dp_{ext} = đq + đw + p_{ext}dV + V dp_{ext}, \text{ no } pV \text{ work}$$

$$dH = đq + đw_{nonpV} + V dp_{ext}, \text{ no } pV \text{ work}$$

When no gases are involved, pV work is usually pretty close to zero, making the change in enthalpy very close to the change in internal energy. In the case where the reaction is occurring

Chapter 6: Thermodynamics Derivations

in open air, where dp=0, and in the absence of any work, we find the following, which is approximately true for most solids and liquids over small temperature ranges:

$$dH = đq \approx dU, \text{little to no change in volume}, p_{ext} \text{ is constant, and } pV \text{ work only}$$

The $p_{ext}dV$ term is equal to zero, because when there is no pV work, either the external pressure p is zero, or the volume is constant, making the dV_{ext} equal to zero. Thus, we see that if there is no change in volume, or if the gas is expanding into free space for an ideal gas, there is no work done.

Change in Enthalpy at Constant Pressure, Along with Coffee Cup Calorimeter Equations and Approximations

Likewise, we have a constant pressure heat capacity, C_p. C_p is equal to:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_{p,n}$$

We can therefore substitute in as follows:

$$đq = \left(\frac{\partial H}{\partial T}\right) dT = C_p dT$$

$$dH = dU + Vdp_{ext} = đq + Vdp_{ext}, pV \text{ work only}$$

$$dH = C_p dT + Vdp_{ext}, pV \text{ work only}$$

$$\Delta H = \int_1^2 đq + \int_1^2 Vdp_{ext} = \int_1^2 C_p dT + \int_1^2 Vdp_{ext}, pV \text{ work only}$$

Here again, we see that to apply the integral, T can only change when V is held constant, and V can only change when T is held constant. In the special case of constant pressure, and pV work only:

$$dH = C_p dT = q, p \text{ is held constant}, pV \text{ work only}$$

$$\Delta H = \int_1^2 C_p dT + \int_1^2 V * 0 = \int_1^2 C_p dT + 0 = \int_1^2 C_p dT, p \text{ is held constant}, pV \text{ work only}$$

Chapter 6: Thermodynamics Derivations

At constant pressure, and small temperature changes,

$$\Delta H = \int_1^2 C_p dT \approx C_p \Delta T \approx mc_p \Delta T,$$

approximating that heat capacity is roughly constant. Pressure is kept constant.

Change in Enthalpy at Constant Volume

In the case of constant volume, to find the change in enthalpy we do the following:

$$dU = đq \text{ in bomb calorimeter, because constant volume}$$

$$dH = dU + d(p_{ext}V) = dU + p_{ext}dV + Vdp_{ext} + dVdp_{ext}$$
$$= dU + p_{ext}dV + Vdp_{ext}, pV \text{ work only}$$

And then, doing:

$$dH = dU + Vdp_{ext} = đq + Vdp_{ext} = C_V dT + Vdp_{ext}, pV \text{ work only}, V \text{ is kept constant}$$

$$\Delta H = \int_1^2 C_V dT + \int_1^2 Vdp_{ext}, pV \text{ work only}, V \text{ is kept constant}$$

Since volume is kept constant in the bomb calorimeter, V is a constant, and we have:

$$\Delta H = \int_1^2 C_V dT + V\Delta p_{ext}, pV \text{ work only}, V \text{ is kept constant}$$

Then finally concluding, with an approximation, that C_V is relatively constant over small intervals of temperature, we have:

$$\Delta H = \int_1^2 C_V dT + V\Delta p_{ext} \approx C_V \Delta T + V\Delta p_{ext},$$

approximating that heat capacity is roughly constant, pV work only, V is kept constant

Change in Internal Energy at Constant Pressure

Now, we apply internal energy to constant pressure situations:

Chapter 6: Thermodynamics Derivations

$$dH = dU + d(p_{\text{ext}}V)$$

$$dU = dH - d(p_{\text{ext}}V)$$

$$dU = dH - Vdp_{\text{ext}} - p_{\text{ext}}dV - dp_{\text{ext}}dV = dH - Vdp_{\text{ext}} - p_{\text{ext}}dV$$

We now have:

$$\Delta U = \int_1^2 dU = \int_1^2 dH - \int_1^2 Vdp_{\text{ext}} - \int_1^2 p_{\text{ext}}dV$$

Since we are keeping pressure constant, we get:

$$\Delta U = \int_1^2 dU = \int_1^2 dH - \int_1^2 V * 0 - \int_1^2 p_{\text{ext}}dV = \int_1^2 dH - 0 - p_{\text{ext}}\Delta V, p_{\text{ext}} \text{ is constant}$$

And, since $dH = đq$ when pressure is constant, we have:

$$\Delta U = \int_1^2 dH - p_{\text{ext}}\Delta V = đq - p_{\text{ext}}\Delta V = \int_1^2 C_p dT - p_{\text{ext}}\Delta V,$$

$$\text{pressure is constant, } pV \text{ work only}$$

Making the approximation that C_p is relatively constant over small temperature ranges, we get a similar expression:

$$\Delta U = \int_1^2 C_p dT - p_{\text{ext}}\Delta V \approx C_p \Delta T - p_{\text{ext}}\Delta V$$

Again, using enthalpy is a lot easier when you have constant pressure. Here, like previously, we can simplify some more. Because the system is in open air, the pressure is pretty much constant inside and outside the system at all times. Thus, we could have just used p instead of p_{ext} in the derivation above.

Converting Between Change in Internal Energy and Change in Enthalpy for an Ideal Gas

We begin with our definition of enthalpy, to find a relation between the change in enthalpy and change in internal energy for an ideal gas:

Chapter 6: Thermodynamics Derivations

$$H = U + pV$$

We write it in differential form:

$$\mathrm{d}H = \mathrm{d}U + \mathrm{d}(pV)$$

We integrate:

$$\int_1^2 \mathrm{d}H = \int_1^2 \mathrm{d}U + \int_1^2 \mathrm{d}(pV)$$

We get the following, which we can easily work with, to relate changes in internal energy and changes in enthalpy for an ideal gas:

$$\Delta H = \Delta U + \Delta(pV)$$

We introduce our ideal gas equation:

$$pV = nRT$$

Now, we write it in differential form:

$$d(pV) = d(nRT)$$

We integrate:

$$\int_1^2 pV = \int_1^2 nRT$$

We get the following:

$$\Delta(pV) = \Delta(nRT), \text{for ideal gases}$$

Now, we have something that we can substitute in.

$$\Delta H = \Delta U + \Delta(pV)$$

$$\Delta H = \Delta U + \Delta(nRT), \text{ideal gases only}, \Delta n \text{ is the change in number of moles of GAS}$$

Thus, using the two equations that we obtained above, we can obtain the following result, if temperature is held constant. R is the molar gas constant.

$$\Delta H = \Delta U + (\Delta n)RT, \text{where temperature is held constant}$$

Chapter 6: Thermodynamics Derivations

We find that for an ideal gas, when temperature is held constant, the change in internal energy is smaller than the change in enthalpy when the number of moles of gas increases, and vice versa. This is because when the number of moles of gas increases, some energy is expended by doing work. Thus, if we know the balanced equation, we can approximately convert between changes in enthalpy and changes internal energy if we are assuming ideal gas behavior. Note that the Δn is the change in number of moles of gas, as change in volume of liquids and solids are relatively insignificant.

The Clausius Inequality: Classical Entropy for Heat Engines

The following inequality is the mathematical statement of the Clausius inequality. Note the inexact differential.

$$\mathrm{d}S \geq \frac{\delta q}{T}$$

Here I used the δ symbol instead of the đ symbol, but both mean inexact differentials. I just used the traditional symbol, because that was how it was written in the 1800's. The equation means that the change in entropy is greater than the heat exchange, divided by the temperature, for heat transferred at a given temperature. The equality holds, in the impossible case of a reversible process. The Clausius inequality is considered to be the classical entropy formula for a heat engine. When we integrate the inequality above, we get the following:

$$\Delta S = \int_1^2 \mathrm{d}S \geq \int_1^2 \frac{\delta q}{T}$$

$$\Delta S = S_2 - S_1 \geq \int_1^2 \frac{\delta q}{T}$$

Note that this integral is very path dependent, as it includes an inexact differential, and a conditional inequality.

Chapter 6: Thermodynamics Derivations

The Helmholtz Free Energy, A

A Derivation of the Helmholtz Free Energy, A

We can derive the Helmholtz free energy using conditions of spontaneity. What we are seeking is a condition to be met for a reaction at constant temperature and constant volume to be spontaneous. We begin from the sum of total entropy, and apply the Clausius inequality to both the system (our atoms and molecules), and the surroundings (the rest of the universe). Thus, we have:

$$dS_{universe} = dS_{system} + dS_{surroundings}$$

We know that the total change in entropy of the universe is always positive, for any spontaneous reaction. Thus, we have:

$$dS_{sys} + dS_{surr} \geq 0$$

Since we have a constant temperature and volume restriction, we can do a substitution. Note that in the universe, whatever receives the energy increases in entropy. When you boil water, the water receives the heat energy, and it becomes relatively disturbed. Since the volume is constant, there is no pV work. In the absence of all other forms of work, the only transfer of energy between the system and the surroundings is by heat. Thus, we substitute in the Clausius inequality as follows, where temperature and volume are kept constant.

$$dS_{sys} - \frac{đq_{rxn}}{T} \geq 0$$

Note the negative sign. Because of the conservation of energy, whatever energy that is lost by the system is given to the surroundings, and whatever energy the system gains is lost by the surroundings. From the perspective of the surroundings, the exact opposite of what happens to the system happens to the surroundings. Thus, we negate the heat of the reaction when we look from the perspective of the surroundings. Since the heat is transferred at constant volume, we can substitute out the inexact differential for the exact differential of a state function:

$$dS_{sys} - \frac{dU_{sys}}{T} \geq 0, constant\ Volume$$

Chapter 6: Thermodynamics Derivations

Note that now everything is written in terms of the system! We happily move everything to the right, put the inequality in a convenient form, and call our condition for spontaneity our Helmholtz free energy.

$$0 \geq \frac{dU_{sys}}{T} - dS_{sys}, \text{Constant Volume}$$

$$0 \geq dU_{sys} - TdS_{sys}, \text{Constant Volume}$$

Now, we define:

$$dA = dU_{sys} - TdS_{sys}$$

$$dA \leq 0 \text{ for spontaneous rxns at constant } T, V$$

Or, for a more familiar form, we integrate:

$$\int dA = \int dU_{sys} - \int TdS_{sys}$$

$$A = U - TS$$

$$\Delta A = \Delta U - \Delta(TS)$$

And, where T is kept constant, we get:

$$\Delta A = \Delta U - T(\Delta S), \text{where } T \text{ is kept constant}$$

A Second Derivation of the Helmholtz Free Energy

From here on, we'll just use p for pressure. It's easier to write, and the basic proofs are pretty much done. Also, there really isn't much difference between p and p_{ext}, because the two are nearly equal before and after the reaction, except for the fact that external pressure is easier to measure. To find the Helmholtz free energy, we do the following:

From the Clausius inequality, we have:

$$dS \geq \frac{đq}{T}$$

$$TdS \geq đq$$

Chapter 6: Thermodynamics Derivations

From the definition of internal energy, we have:

$$dU = đq + đw$$

Now, we substitute in for the $đq$. However, note that we result in an inequality. The value we substitute in will be greater than the original value, as entropy is greater than or equal to in the Clausius statement. I rearranged, to make it easier for you to see.

$$dU - đw = đq$$

$$dU - đw \leq TdS$$

In this inequality, we see that the temperature is always positive. Then, we apply an identity:

$$d(TS) = SdT + TdS + dSdT$$

This is very similar to what we saw previously with $d(pV)$, and it is for the same reason why we simplify the identity above to:

$$d(TS) = SdT + TdS \text{ for all finite things}$$

Therefore, adding SdT-SdT is equal to adding zero. However, it allows us to rearrange the equation:

$$dU - đw \leq TdS + SdT - SdT$$

$$dU - đw \leq d(TS) - SdT$$

$$dU - d(TS) \leq -SdT + đw$$

Combining the left side, we obtain:

$$d(U - TS) \leq -SdT + đw$$

We define the change in the Helmholtz free energy to be equal to the left side:

$$dA = d(U - TS) \leq -SdT + đw$$

Not only are the increments equal to each other. The relation holds true as follows, which is the formal relation of internal energy and the Helmholtz free energy:

$$dA = dU - d(TS)$$

Chapter 6: Thermodynamics Derivations

$$dA \leq 0 \text{ for spontaneous rxns, constant } T, V$$

$$\Delta A = \Delta U - \Delta(TS)$$

Or, in general:

$$A = U - TS$$

And, at constant temperature,

$$\Delta A = \Delta U - T\Delta S$$

Physical Interpretation of the Helmholtz Free Energy, and Conditions for Spontaneity

Thus, if we move the right of the above inequality $dA = d(U - TS) \leq -SdT + đw$ over, we get our condition that allows for us to determine whether or not a reaction is possible at a given temperature, the definition of the Helmholtz free energy, and the meaning of free energy:

$$d(U - TS) + SdT - đw = dA + SdT - đw \leq 0$$

Overall, if we just integrate, we get the following:

$$\int_1^2 dU - \int_1^2 d(TS) + \int_1^2 SdT - \int_1^2 đw = \int_1^2 dA + \int_1^2 SdT - \int_1^2 đw \leq 0$$

$$\Delta U - \int_1^2 TdS - \int_1^2 SdT + \int_1^2 SdT - w = \int_1^2 dA + \int_1^2 SdT - w$$

$$\Delta U - \int_1^2 TdS - w = \Delta A + \int_1^2 SdT - w \leq 0$$

Thus, we see that for the Helmholtz free energy, if there is no restriction on the type of process, we have the following:

$$\Delta A = \Delta U - \int_1^2 TdS - \int_1^2 SdT = \Delta U - \int_1^2 TS = \Delta U - \Delta(TS) \leq -\int_1^2 SdT + w$$

However, the equation is more useful when in some specific situations. For example, integrating at constant temperature instead, we get:

Chapter 6: Thermodynamics Derivations

$$\Delta U - \int_1^2 T dS - \int_1^2 đw = \int_1^2 dA + \int_1^2 S * 0 - \int_1^2 đw$$

$$\Delta U - T\Delta S - w = \Delta A - w \leq 0$$

And, in the case of constant temperature and volume, we get the following:

$$U - T\Delta S - w_{nonpV} = \Delta A - w_{nonpV} \leq 0, T \text{ and } V \text{ are constant}$$

If all the work is pV work, and the temperature and volume is constant, then $đw=-pdV$, $dV=0$, and work is equal to zero. Thus, the Helmholtz free energy is equal to the following when there is only pV work, and volume is constant, because then $w=0$:

$$\Delta U - T\Delta S = \Delta A \leq 0, T, V \text{ constant}, pV \text{ work only}$$

Since the change in internal energy is equal to the heat transfer at constant volume, we can quickly check the correctness of the statement using the Clausius inequality:

$$đq \leq T dS$$

$$q \leq T\Delta S$$

$$\Delta A = q - T\Delta S \leq 0, T, V \text{ constant}, pV \text{ work only}$$

Thus, we see that for a reaction at constant temperature and volume to be possible, the Helmholtz free energy must be negative. This is an easy check for the spontaneity of a reaction, because a possible, spontaneous reaction at constant temperature and volume must have a negative value of change in the Helmholtz free energy.

If we drop the constant volume requirement, and apply the isothermal restriction, we can get the following, which is the meaning of free energy:

$$\Delta U - T\Delta S - w = \Delta A - w \leq 0$$

Then, we move the w to the other side.

$$\Delta A = \Delta U - T\Delta S \leq w$$

Chapter 6: Thermodynamics Derivations

Thus, the Helmholtz free energy is the maximum amount of possible work that a reaction can do at constant temperature. Note that for all possible reactions, the Helmholtz free energy must be negative. Since work done by a system is considered NEGATIVE work, the w on the right side is also negative. Thus, the w is a less negative negative than the Helmholtz free energy.

$$\Delta A \leq w_{\text{max that can be done by system}}$$

The work we can obtain from the system, which is the maximum work the system can do, is equal to:

$$\Delta A \leq w_{\text{max that can be done by system}} = -w_{\text{we can obtain}}$$

Thus, the negative of the Helmholtz free energy is the most amount of work we can obtain from the system.

$$-\Delta A \geq w_{\text{we can obtain}} = -w_{\text{done by system}}$$

Note that now, the inequality has flipped, because we multiplied by a -1. This means that the change in Helmholtz free energy is equal to the maximum theoretical amount of work the system can perform. Therefore, the Helmholtz free energy is represented by A, for Arbeitsfunktion. Thus, in a reversible process, the actual amount of work performed is equal to the change in the Helmholtz free energy. However, reversible processes are impossible. Therefore, for all real, irreversible reactions and processes, the amount of work that we can get is less than the maximum theoretical work, which is the Helmholtz free energy. Note that this is only for the case of constant temperature. For other situations, we would need to set up a thermochemical cycle, and sum up the net work done for each step. In the case of constant temperature and volume, we get the amount of non pV work the system can do. In the case of pV work only, at constant temperature, we can substitute in:

$$\Delta A = \Delta U - T\Delta S \leq \int_1^2 đw$$

$$đw = -pdV$$

$$\Delta A = \Delta U - T\Delta S \leq - \int_1^2 pdV$$

Chapter 6: Thermodynamics Derivations

And, adding the restriction of constant pressure leads us to:

$$\Delta A = \Delta U - T\Delta S \leq -p\Delta V, T, p \ constant, pV \ work \ only$$

A Fundamental Thermodynamic Relation That We Had as an Intermediate in Our Derivation

An identity that we had as an intermediate byproduct in the derivation, that would be useful later, is the following relation that applies when all the work is pV:

$$\mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V$$

It stems from the definition that:

$$\mathrm{d}A = \mathrm{d}U - \mathrm{d}(TS)$$

And when only pV work is allowed,

$$\mathrm{d}A = đq + đw - T\mathrm{d}S - S\mathrm{d}T - \mathrm{d}T\mathrm{d}S$$

And then, cancelling out the $\mathrm{d}T\mathrm{d}S$, then using the Clausius Inequality and substituting in for $đq$, and then substituting in $-p\mathrm{d}V$ for $đw$, we get:

$$\mathrm{d}A = T\mathrm{d}S - p\mathrm{d}V - T\mathrm{d}S - S\mathrm{d}T = -S\mathrm{d}T - p\mathrm{d}V$$

$$\mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V$$

The Gibbs Free Energy, G

A Derivation of the Gibbs Free Energy, G

We can derive the Gibbs free energy using conditions of spontaneity. What we are seeking is a condition to be met for a reaction at constant temperature and constant pressure to be spontaneous. We begin from the sum of total entropy, and apply the Clausius inequality to both the system (our atoms and molecules), and the surroundings (the rest of the universe). Thus, we have:

$$\mathrm{d}S_{universe} = \mathrm{d}S_{system} + \mathrm{d}S_{surroundings}$$

We know that the total change in entropy of the universe is always positive, for any spontaneous reaction. Thus, we have:

$$dS_{sys} + dS_{surr} \geq 0$$

Since we have a constant temperature and volume restriction, we can do a substitution. Note that in the universe, whatever receives the energy increases in entropy. When you boil water, the water receives the heat energy, and it becomes relatively disturbed. Thus, we substitute in the Clausius inequality as follows, where temperature and pressure is kept constant.

$$dS_{sys} - \frac{đq_{rxn}}{T} \geq 0$$

Note the negative sign. Because of the conservation of energy, whatever energy that is lost by the system is given to the surroundings, and whatever energy the system gains is lost by the surroundings. Thus, we negate the heat of the reaction when we look from the perspective of the surroundings. If the heat is transferred at constant pressure, we can substitute out the inexact differential for the exact differential of a state function:

$$dS_{sys} - \frac{dH_{sys}}{T} \geq 0$$

Note that now everything is written in terms of the system! We happily move everything to the right, put the inequality in a convenient form, and call our condition for spontaneity at constant temperature and pressure our Gibbs free energy.

$$0 \geq \frac{dH_{sys}}{T} - dS_{sys}$$

$$0 \geq dH_{sys} - TdS_{sys}$$

Thus, we define:

$$dG = dH_{sys} - TdS_{sys}$$

$$dG \leq 0 \text{ for spontaneous rxns at constant } T, p$$

Or, for a more familiar form, we integrate:

Chapter 6: Thermodynamics Derivations

$$\int dG = \int dH_{sys} - \int T dS_{sys}$$

$$G = H - TS$$

$$\Delta G = \Delta H - \Delta(TS)$$

$$\Delta G = \Delta H - T(\Delta S), \text{where } T \text{ is kept constant}$$

A Second Derivation of the Gibbs Free Energy

For the Gibbs free energy, we do a similar derivation as we did before, for the Helmholtz free energy. This time, we begin with the enthalpy formula:

$$H = U + pV$$

Differentiating both sides, we get:

$$dH = dU + d(pV) = dU + pdV + Vdp + dpdV = đq + đw + pdV + Vdp$$

Likewise, substituting in for the change in heat by means of the Clausius inequality produces:

$$dH \leq TdS + đw + pdV + Vdp$$

Substituting in the same identity as before, we add 0=SdT-SdT to both sides.

$$dH \leq TdS + SdT - SdT + đw + pdV + Vdp$$

$$dH \leq d(TS) - SdT + đw + pdV + Vdp$$

We now arrive at:

$$dH - d(TS) \leq -SdT + đw + pdV + Vdp$$

$$d(H - TS) \leq -SdT + đw + pdV + Vdp$$

Here, we notice that we have the same type of relation as before. Therefore, we define G to be equal to:

$$G = H - TS$$

And therefore:

Chapter 6: Thermodynamics Derivations

$$dG = dH - d(TS)$$

$$\Delta G = \Delta H - \Delta(TS)$$

And, at constant temperature,

$$\Delta G = \Delta H - T\Delta S$$

Physical Interpretation of the Gibbs Free Energy, and Conditions for Spontaneity

We continue with:

$$dG = d(H - TS) \leq -SdT + đw + pdV + Vdp$$

$$dG + SdT - đw - pdV - Vdp = d(H - TS) + SdT - đw - pdV - Vdp \leq 0$$

Here, notice that we still have the Vdp and the pdV. The reason why we expanded it is so that the integration portion makes more sense. Note that we can make terms disappear, by having constant temperature, constant volume, constant pressure, and by restricting the work to pV only. However, do note that the relation between the Helmholtz and the Gibbs free energies are as follows:

$$\Delta A + \Delta(pV) = \Delta U - \Delta(TS) + \Delta(pV) = \Delta(U + pV) - \Delta(TS) = \Delta H - \Delta(TS) = \Delta G$$

Now, we go on to integrating, to find the special properties of the Gibbs free energy.

$$dG = d(H - TS) \leq -SdT + đw + pdV + Vdp$$

If we just integrate straight, we get a bunch of integrals that we can't really use, much like in the case of the Helmholtz equation earlier.

$$\Delta G = \int_1^2 dH - \int_1^2 d(TS) = \int_1^2 dH - \int_1^2 SdT - \int_1^2 TdS$$

$$\leq \int_1^2 -SdT + \int_1^2 đw + \int_1^2 pdV + \int_1^2 Vdp$$

$$\Delta G = \Delta H - \Delta(TS) = \int_1^2 dH - \int_1^2 SdT - \int_1^2 TdS \leq \int_1^2 -SdT + \int_1^2 đw + \int_1^2 pdV + \int_1^2 Vdp$$

Chapter 6: Thermodynamics Derivations

However, we can do the following. If we restrict the processes to isothermal, we get:

$$\Delta G = \Delta H - T\Delta S = \int_1^2 dH - \int_1^2 S*0 - \int_1^2 TdS \leq \int_1^2 -S*0 + \int_1^2 đw + \int_1^2 pdV + \int_1^2 Vdp$$

$$\Delta G = \Delta H - T\Delta S \leq \int_1^2 đw + \int_1^2 pdV + \int_1^2 Vdp$$

That is still not quite useful. However, by adding the restriction of constant pressure, we get:

$$\Delta G = \Delta H - T\Delta S \leq \int_1^2 đw + \int_1^2 pdV + \int_1^2 V*0$$

$$\Delta G = \Delta H - T\Delta S \leq \int_1^2 đw + p\Delta V$$

Since $p\Delta V$ is equal to $-w_{pV}$, we find that the Gibbs free energy is equal to the non-pV work when the temperature and pressure are constant, because the pV work is subtracted out from the total work, on the right side. Likewise, for all possible reactions, the Gibbs free energy is negative, and work done by the system is negative.

$$\Delta G \leq w_{\max\,non-pV,\text{done by the system}} = -w_{\max\,non-pV}, at\ constant\ p\ and\ T$$

Thus, a similar argument holds for the Gibbs free energy. However, there is one extra restriction in the work output calculated, which is that in the Gibbs free energy, pressure is constant. Likewise, if we apply the pV work only restriction, we get:

$$\Delta G = \Delta H - T\Delta S \leq 0, \text{for spontaneous, possible rxn.}\ T, p\ \text{held constant}$$

In the case of constant volume, we arrive at

$$\Delta G = \Delta H - T\Delta S \leq \int_1^2 đw + \int_1^2 p*0 + \int_1^2 Vdp, V\ \text{held constant}, T\ \text{held constant}$$

This means that all the work is non-pV. Then, imposing the constant pressure also, we get:

$$\Delta G = \Delta H - T\Delta S \leq \int_1^2 đw, \text{all work is non} - pV, \text{because of constant Volume}$$

Chapter 6: Thermodynamics Derivations

$$\Delta G = \Delta H - T\Delta S \leq w_{\text{non}-pV}, \text{where all work is } non - pV, \text{because } p, T, \text{and } V \text{ held constant}$$

However, we found our previous case of constant temperature and pressure to be more useful, because it was more general than the very limited case of constant temperature, volume and pressure. Thus, we already know, that at constant pressure and temperature, the Gibbs free energy is a measure of the total amount of non-pV work the system can do.

Another Fundamental Thermodynamic Relation We Had as an Intermediate.

Using the useful byproduct that we had earlier, and the relation between dA and dG, we have the following, another useful fundamental relation, which is valid when there is only pV work:

$$dA = -SdT - pdV$$

$$dA + d(pV) = dG$$

$$dA + pdV + Vdp = dG$$

$$-SdT - pdV + pdV + Vdp = dG$$

Therefore, we have:

$$dG = -SdT + Vdp$$

We can see that imposing pV work only on the previous equation:

$$dG = d(H - TS) \leq -SdT + đw + pdV + Vdp$$

Results in the same expression, because then there is no more work on the right side, and only the -SdT and the Vdp remain.

Comparing the Helmholtz and Gibbs Free Energies

When we compare and relate the Gibbs and Helmholtz free energies, we find that subtracting the Gibbs free energy from the Helmholtz free energy when the temperature and

Chapter 6: Thermodynamics Derivations

pressure are constant, yields the amount of pV work that occurs for a reaction. This is shown below:

$$dA + d(pV) = dG$$

$$dA - dG = -d(pV)$$

$$dA - dG = -Vdp - pdV$$

In the case of constant pressure, this results in:

$$dA - dG = -V * 0 - pdV, \text{constant } T, p$$

Thus,

$$dA - dG = -pdV = dw_{pV}, \text{constant } T, p$$

And finally,

$$\Delta A - \Delta G = -p\Delta V = w_{pV}, \text{constant } T, p$$

Likewise, since we have the following relations that we had before:

$$\Delta G = \Delta H - T\Delta S \leq w_{\text{max non}-pV}, \text{constant } p, \text{constant } T$$

$$\Delta A = \Delta U - T\Delta S \leq w_{\text{max all work}}, \text{constant } T$$

Thus,

$$\Delta A - \Delta G = \Delta U - T\Delta S - \Delta H + T\Delta S$$

Since the term causing the inequality, TΔS, is cancelled out, the inequality becomes an equality!

$$\Delta A - \Delta G = \Delta U - \Delta H = w_{\text{max}} - w_{\text{non}-pV \text{ max}}$$

And because we imposed constant temperature and pressure, but not pV work only, we can separate the change in internal energy, and also have the following:

$$dU = đq + đw_{\text{non}-pV} + đw_{pV}$$

$$dH = dU + d(pV) = dU + pdV + Vdp + dpdV$$

Chapter 6: Thermodynamics Derivations

$$dH = đq + đw_{\text{non}-pV} + đw_{pV} + pdV + Vdp$$

$$dH = đq + đw_{\text{non}-pV} + đw_{pV} - dw_{pV} + Vdp$$

$$dH = đq + đw_{\text{non}-pV} + Vdp$$

And, applying constant pressure, we get:

$$dH = đq + đw_{\text{non}-pV} + 0 = đq + đw_{\text{non}-pV}$$

Thus,

$$\Delta A - \Delta G = \Delta U - \Delta H = q + w_{pV} + w_{\text{non}-pV} - q = w_{pV}, \text{for constant } T, p$$

Thus, we finish the derivation! Kewl, eh?

Fundamental Thermodynamic Relations

Just know how to convert between U, H, S, A and G if you are asked to. Also, remember the special intermediates? It turns out that you can express U, H, and S likewise. In fact, you have already encountered the relations for U and H. These relations are important, as they allow us to relate the state functions and variables with respect to one another, without needing to use values that are nonholonomic (path dependent), such as inexact differentials, and makes life easier. However, these relations were developed for pV work only, as we seen before, and have some restrictions.

For U:

$$U = q + w$$

$$dU = đq + đw$$

For pV work only, and only equal if process is reversible:

$$dU \leq TdS - pdV$$

For H, pV work only, and equal if process reversible:

Chapter 6: Thermodynamics Derivations

$$H = U + pV$$

$$\mathrm{d}H = \mathrm{d}U + \mathrm{d}(pV)$$

$$\mathrm{d}H \leq T\mathrm{d}S - p\mathrm{d}V + p\mathrm{d}V + V\mathrm{d}p = T\mathrm{d}S + V\mathrm{d}p$$

For A, as proven earlier,

$$\mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V$$

For G, as proven earlier,

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p$$

For S, we can just solve for S, in any of the above relations, but equality again only holds for reversible processes. Using these fundamental relations, we can also derive many other equations, which we will not do here. However, you should think of all the thermodynamic quantities as dependent upon each other, because changing one variable usually changes one or more of the other variables, because changing one variable causes a change in state. However, be careful to pay close attention to the restrictions, such as pV work only, or something kept constant, or reversible process, etc, because certain relations may only be applied in certain circumstances.

Ideal Thermodynamic Processes for Ideal Gases:

For ideal gases, it is very easy to relate the state variables to one another. Since all the variables are related by the ideal gas law, $pV=nRT$, we can replace some quantities with equivalent forms. Thus, it is very convenient to illustrate the basic types of ideal processes with an ideal gas. The basic types of ideal processes that are commonly encountered are compressions, expansions, heating, and cooling with some variable held constant. Thus, we have the:

1. Adiabatic expansion and compression, where the walls of the system do not permit heat to enter nor exit. In this case, there is no change in energy by heat, although the gas will

Chapter 6: Thermodynamics Derivations

heat up. We control the pressure, and restrict transfer of heat. Thus, dq, and therefore, q, is equal to zero. Also, if the system only undergoes reversible processes, and there are no dissipative forces, and the external environment is stable, the entropy of the system is constant, making it isentropic.

2. Isochoric heating and cooling, where the volume of the system is held constant. In this case, there is no pV work, and the pressure changes as heat is added or taken away. Thus, if all the work is pV work, đw=0 and therefore, w=0. We control the amount of heat, and restrict the gas from expanding and compressing.

3. Isobaric heating and expansion, or cooling and compression, where the pressure is held constant. Here, all pV work can be described by the equation w=-$p\Delta V$, because p does not change. For this one, there are two paired variables that both must change, being temperature, and volume. If we heat the system, we must expand, and if we cool the system, we must compress, and vice versa to keep the pressure constant. We control both heat and volume, to keep the pressure constant.

4. Isothermal compression and expansion, where the temperature is held constant. There are three ways to bring about isothermal processes, and one is far easier than the other two. The first two ways we can keep the temperature constant, is to increase the pressure while simultaneously increasing the volume, or decrease the pressure while simultaneously decreasing the volume. Both are physically impossible. The easy way is to just immerse the system in a constant temperature bath that ensures that temperature is fairly constant. For all intents and purposes, to keep the system isothermal, we need to have a bath sufficiently large so that drawing or releasing heat into it doesn't change the temperature of the bath. Thus, in other words, we need a bath with infinite heat capacity. We make this idealization when we submerge reaction vessels in constant temperature baths in the lab. The energy and enthalpy of an ideal gas only depends on the temperature of the gas. Therefore, for isothermal processes, the work is equal to the negative of the heat, (đq=-đw, thus q=-w). If there is only pV work, then q=pdV.

5. Isentropic processes. Now we are breaking the second law, because this is a system in which entropy stays constant, no matter what happens. However, in an ideal system, this is possible! We can have a system that is adiabatic, frictionless, dragless, and dissipativeforceless, which only undergoes reversible processes. This is so ridiculous,

that I made up a word for it! No heat transferred in adiabatic systems mean that đq=0, and reversible processes mean that the Clausius statement is equivalent on both sides. Thus, we have change in entropy, dS, equal to zero as well! Oh, did I forget? Because of the restrictions of the system, everything done by this system is 100% efficient, which as we know, is impossible. In an isentropic system, only reversible compression and expansion is allowed, because the system only does reversible processes inside imaginary adiabatic walls.

Using these ideal processes, we can calculate the change in the state variables and functions no matter what possible state the ideal gas system is at. Since the state variables and functions do not care what path we take, we just connect the first state to the second state on a p, V, T graph using these ideal processes, which always travel parallel to one of the axes, and go to town. There are other paths that you can take, but they are nearly impossibly hard. Notice that decomposing a complicated process into the sum of a few of these ideal processes simplifies the problem to the point where we can actually calculate what happens. However, the ideas of these ideal processes are good to know and keep in mind, because they are significant in that they provide us the ability to analyze separate components of problems. This idea of breaking up the problem into pieces will show up repeatedly, so get used to it.

The Person-Kirchhoff Law

The change in enthalpy for a reaction does vary depending on the temperature the reaction is carried out, as determined experimentally and published by Charles Cléophos Person in his 1851 paper "Specific Heats of Salt Solutions." Person used the difference in enthalpy of dissolutions at various temperatures of many salts, in order to come up with an empirical relation between the two.

$$\text{Person's Equation:} \quad q + \left[\frac{k + p}{1 + p} - c \right](1 + p)\theta = q_0$$

Where q is the amount of heat absorbed or released by the dissolution of the salt at the current temperature in calories, q_0 is the amount of heat absorbed or released by the dissolution of the salt at zero degrees centigrade (Celsius) in calories, k is the specific heat capacity of the salt in

Chapter 6: Thermodynamics Derivations

calories per Celsius, c is the specific heat capacity of the solution in calories per Celsius, p is the number of grams of water per gram of salt, and θ is the temperature in Celsius at which the salt is dissolved. Remember that water has a specific heat capacity of 1 calorie, meaning that $1 \text{ cal} = 4.184 \text{ J}$ can raise a gram of water by approximately $1\,°C$. Although this may be confusing, Person's equation can be rearranged, to get the following:

$$-q = -q_0 + [(k + p) - c(1 + p)]\theta$$

Remember that the dissolution in this case was carried out in an open air constant pressure calorimeter. Thus, the change in heat is equal to the change in enthalpy. Since k and c are both heat capacities in calorie per Celsius, the term $k+p$ is just equal to the specific heat of the solid salt, plus the specific heat of the water, which are the reactants. Likewise, $c(1 + p)$ is just equal to the specific heat of the solution, multiplied by the density of water, 1, plus the grams of water per gram of salt. This yields the heat capacity of the final products of dissolution. The temperature here is relative to zero degrees Celsius, and the temperature range over which the experiment was carried out is sufficiently small that deviations were not significant. Thus, rewriting the equation, we get the following, where the superscripted plimsoll $\ominus$ indicates STP:

$$-\Delta H_T = -\Delta H^{\ominus} + (C_r - C_{pr})(T - 273.15 \text{ K})$$

$$\Delta H_T = \Delta H^{\ominus} + (C_{pr} - C_r)\theta = \Delta H^{\ominus} + (C_{pr} - C_r)(T - 273.15 \text{ K})$$

This translates to, in words, that the

Change in enthalpy of the reaction at a temperature given in Celsius	Is equal to	The Change in enthalpy of the reaction at zero degrees Celsius (STP, T=273.15 K)	Plus	Difference between the heat capacity of the products and the reactants	Times	The temperature at which the change takes place, in degrees Celsius
ΔH_T	=	$\Delta H^{\ominus}$	+	$(C_{pr} - C_r)$	*	θ

Note that the changes in enthalpy are in calories, and the heat capacities in Person's formula are in calories per degree Celsius. However, as we will see with Kirchhoff's formula, the

Chapter 6: Thermodynamics Derivations
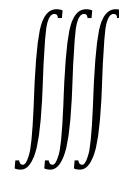
units do not matter. The rearranged Person's equation indicates that the change in enthalpy of dissolution at a given temperature, ΔH_T, is equal to the change of enthalpy of dissolution at Standard Temperature and Pressure (STP, T=273.15 K, p=1 bar), $\Delta H^{\ominus}$, plus the product of the temperature in Celsius, θ, and the difference between the heat capacities of the products and the reactants, $(C_{pr} - C_r)$. All this means, is that if the sum of the heat capacities of the products is less than that of the reactants $(C_{pr} < C_r)$, conducting the reaction at a lower temperature leads to an increase in change of enthalpy, and vice versa, which is summarized in the table below:

$C_{pr} - C_r$	Increasing the temperature	Decreasing the temperature
< 0	$\Delta H < \Delta H^{\ominus}$	$\Delta H > \Delta H^{\ominus}$
$= 0$	$\Delta H = \Delta H^{\ominus}$	$\Delta H = \Delta H^{\ominus}$
> 0	$\Delta H > \Delta H^{\ominus}$	$\Delta H < \Delta H^{\ominus}$

Seven years later, in 1858, Gustav Kirchhoff published his law of thermochemistry. Since Kirchhoff's treatment is more mathematically rigorous and physically general, most texts omit "Person" from the Person-Kirchhoff law of thermochemistry.

$$\text{Kirchhoff's Law of Thermochemistry:} \left(\frac{\partial(\Delta H)}{\partial T}\right)_p = C_{pr} - C_r$$

Here, the ∂ only means a small change at constant pressure, which is a condition indicated by the subscripted italic p on the bottom of the parentheses containing the partial derivative. This means that a small change in the change in enthalpy for a reaction, $\partial(\Delta H)$, divided by a small change in the temperature, ∂T, is equal to the difference in the constant pressure heat capacity of the products and the reactants involved in the reaction, $C_{products} - C_{reactants}$. Rearranging, we also get the following, which means that a small change in the change in enthalpy for the reaction, $\partial(\Delta H)$, is equal to the difference in constant pressure heat capacities of the products and the reactants, $C_{pr} - C_r$, multiplied by the small change in temperature, ∂T, that occurs at constant pressure.

Chapter 6: Thermodynamics Derivations

$$\partial(\Delta H) = \left(C_{\text{pr}} - C_{\text{r}}\right) * \partial T, \text{at constant pressure}$$

Although the heat capacities of the products and reactants are not constant because they are not ideal, they vary when the temperature changes. However, if no phase change in the products nor reactants occurs over the temperature range, then the heat capacities are fairly constant. Thus, if we add up all of the changes in heat capacity over a range of temperature, $T_1 \text{ to } T_2$, we get:

$$\Delta(\Delta H) = \Delta H_{T_2} - \Delta H_{T_1} \approx \left(C_{\text{pr}} - C_{\text{r}}\right) * \Delta T$$

Note that this is an approximation which is valid for most practical purposes.

The C_p of a substance is equal to the small change in enthalpy that is required for a small change in temperature at a constant pressure.

At constant pressure, a small amount of enthalpy required for a small change in temperature, ∂H, is equal to that small change in temperature, ∂T, multiplied by the constant pressure heat capacity, C_p.

Therefore,

$$\partial H = C_P \partial T \text{ at constant pressure}$$

And

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

By approximating that the heat capacity is constant over our range of temperature, essentially, we are just saying that the change in enthalpy of the substance due to a change in temperature, ΔH, divided by that change in temperature, ΔT, is equal to a constant.

$$C_p \approx \frac{\Delta H}{\Delta T} = a \; constant$$

Chapter 6: Thermodynamics Derivations

Kirchhoff's equation does not apply when there is a phase change, because at a phase change, the heat capacity of the substance is infinite. That is because there is no change in temperature until the phase change is complete, although there is change in enthalpy.
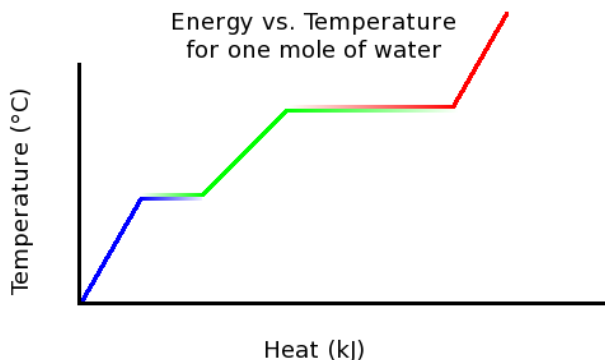
Figure 6.3. A diagram of temperature as heat is added to a sample of water. Note how the temperature does not change during phase changes. Therefore, the heat capacity during a phase change is infinite.

During a phase change, ΔT is equal to zero, whereas ΔH is usually very large, because changes in phase typically are associated with large changes in enthalpy. During the phase change, the following occurs, which makes the equation invalid:

$$\text{During Phase Change,} \frac{dH}{dT} \text{ is infinite, because } dH \neq 0, \text{ and } dT = 0$$

Now, assuming that we do not undergo a phase change in the interval of interest, we compare the rearranged Person's equation and the approximate form of the Kirchhoff equation. We find that they are nearly the same:

$$\text{Approximate form of the Kirchhoff Equation: } \Delta H_{T_2} - \Delta H_{T_1} \approx \left(C_{\text{pr}} - C_{\text{r}}\right) * \Delta T$$

$$\text{Rearranged form of Person's Equation: } \Delta H_T = \Delta H^{\ominus} + \left(C_{\text{pr}} - C_{\text{r}}\right)(T - 273.15\ K)$$

Rearranging Person's equation again:

$$\text{Rearranged form of Person's Equation: } \Delta H_T - \Delta H^{\ominus} = \left(C_{\text{pr}} - C_{\text{r}}\right)(T - 273.15)$$

The rearranged Person's equation is essentially the same as the approximate Kirchhoff Equation, except that the initial temperature, T_1, is set at 273.15 K, or 0 degrees Celsius. If we

Chapter 6: Thermodynamics Derivations

subtract the ΔH_T calculated by the Person's equation at temperature T_2, from the ΔH_T calculated by the Person's equation at temperature T_1, we get the approximate form of the Kirchhoff Equation. Note that the standard enthalpy change for the reaction is a constant, and gets cancelled out. Also, note that the difference of the heat capacities times the standard temperature also gets cancelled out.

$$\left(\Delta H_{T_2} - \Delta H^{\ominus}\right) - \left(\Delta H_{T_1} - \Delta H^{\ominus}\right) = \left(C_{pr} - C_r\right)(T_2 - 273.15\ \text{K}) - (C_{pr} - C_r)(T_1 - 273.15\ \text{K})$$

$$\Delta H_{T_2} - \Delta H_{T_1} - \left(\Delta H^{\ominus} - \Delta H^{\ominus}\right)$$
$$= \left(C_{pr} - C_r\right)T_2 - \left(C_{pr} - C_r\right)T_1 - [\left(C_{pr} - C_r\right)(273.15\ \text{K}) - \left(C_{pr} - C_r\right)(273.15\ \text{K})]$$

$$\Delta H_{T_2} - \Delta H_{T_1} = \left(C_{pr} - C_r\right)(T_2 - T_1) = \left(C_{pr} - C_r\right)\Delta T$$

Thus, although the change in enthalpy for a reaction is not constant, the difference in the heat capacity of the products and the reactants is sufficiently small, and the change in the change of enthalpy is relatively insignificant if the temperature range is small. This approximate form of the Person-Kirchhoff equation is fairly useful, if it ever be necessary to ballpark the change in enthalpy of a reaction that is not carried out at standard temperature. For internal energy, we can do something similar. However, since it is not useful, and we can approximate internal energy from change in enthalpy, there is not much need for us to do so right now.

Chapter 6: Thermodynamics Derivations

Chapter 7: The Structure of the Atom

Subatomic Particles

Chemistry is about the study of matter at the atomic scale. However, to understand the behavior of atoms, we must understand the components of an atom. Atoms consist of 3 main subatomic particles. Properties of the particles are given in the table below. The Dalton is a derived unit, equal to $\frac{1\frac{gram}{mol}}{N_A} = 1.660\ 538\ 921 \times 10^{-27}$ kg, and is also known as the unified atomic mass unit. Charge in this case is measured in multiples of the charge of the electron, e, with one electron charge being equal to $1.602\ 176\ 62 \times 10^{-19}$ C. The electron charge is also known as the elementary electric charge.

Particle	Mass in kg	Mass in Daltons (u)	Charge
Electron	$m_e = 9.109\ 383\ 56 \times 10^{-31}$	0.00054858	-1
Proton	$m_p = 1.672\ 621\ 898 \times 10^{-27}$	1.007276	+1
Neutron	$m_n = 1.674929 \times 10^{-27}$	1.008664	0

Most of the mass of the atom comes from the protons and the neutrons. The mass of the electron is so small, being about 5.4×10^{-4}th of a proton or a neutron, that it is neglected when calculating atomic mass. The number of protons, Z, and the number of neutrons, N, add up to the atomic nucleon number, A. Protons and neutrons are called nucleons because they are inside the nucleus of the atom. When A is multiplied by the unified atomic mass unit, then multiplied by Avogadro's number, we get the mass in kilograms of a mole of that atom. Thus, we see that the nucleon number A is approximately the mass in grams of a mole of that atom, because a mole of the atomic mass unit is approximately 1 gram, or 0.001 kg.

Existence of Isotopes

Isotopes and the Kinetic Isotope Effect

In chemistry, most of the interactions between atoms are due to the electrons, as the electrons have less mass, and are easier to move. Since pure elements are neutral, the number of electrons and protons are the same. However, most of the elements exist in multiple isotopes. Isotopes are atoms that have the same number of protons and electrons, but not the same number of neutrons. Thus, isotopes, because they have the same number of protons and electrons, have nearly identical chemical properties in terms of reactivity, but they differ in their atomic masses. The only element with a significant difference in chemical reactivity is hydrogen, because deuterium (Hydrogen-2) has approximately two times the mass of protium (Hydrogen-1), thus making deuterium far less reactive. Protium is 6-10 times more reactive than deuterium. Tritium is very rare, so it is not used experimentally. In comparison, carbon-12 is only 4% faster at reacting than a corresponding carbon-13, because the mass difference is less significant given the mass of the carbon atoms (1:12). Because it is harder to move objects with more mass, the heavier isotope is bonded more strongly to the molecule. Thus, more energy is required for a reaction to take place when the heavier isotope is present. Many reactions depend on the molecules colliding hard enough to proceed, and increasing the mass decreases the fraction of molecules with sufficient velocity, which in turn, also decreases frequency of collision. The heavier molecules collide slower and less often. This difference in reactivity due to difference in isotope is commonly known as the kinetic isotope effect, because the effect describes the speed, or kinetics, of the reaction.
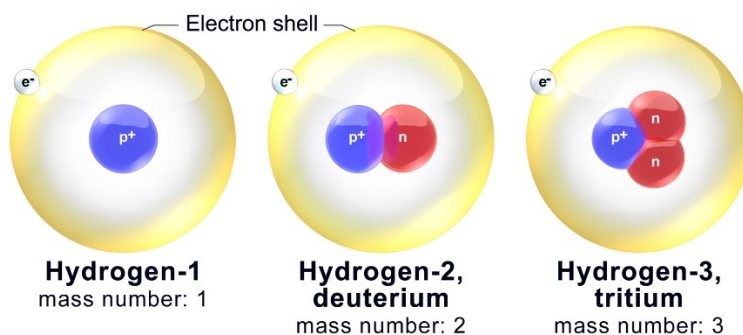
Figure 7.1. A simplified diagram of the three isotopes of hydrogen.

Chapter 7: The Structure of the Atom

Isotopes and the Periodic Table

Now, you may ask, why are the atomic masses on the periodic table not whole numbers, even though for an atom the nucleon number, A, must be an integer? That is because the atomic mass numbers on the periodic table are the average masses of the elements, and that depends on the natural abundance of the isotopes of the element. Since we are on earth, the isotopic composition of an element should be fairly constant everywhere. Therefore, the numbers are somewhat representative of the mass of the element in natural abundances on earth.

Beginnings of Quantization

The concept of quantization will appear numerous times. The very fact that we talk of protons, electrons, and neutrons is the result of quantization. Quantization means that there is a minimum amount, some quanta, that makes up a large amount, a quantity. For example, 10 balls. The quantity would be 10 balls, and the quanta would be 1 ball. 10x1 ball gives you 10 balls. If you cut the ball in half, it would no longer be a ball. Same thing applies to atoms, electrons, neutrons, protons, and many other things. If you have a mole of helium atoms, you have an Avogadro's number of helium atoms. The mole of helium atoms is made up of individual helium atoms. If you divide up a helium atom, you no longer have helium.

Dalton's Early Atomic Theory

We have discussed before, that in 1803, English chemist John Dalton proposed his atomic theory postulates, most of which are still valid 200 years later. Dalton's theory is very important here, because it made the concept of the atom common. Previously, many believed that elements are substances that can be infinitely divided, as Aristotle and Plato had suggested. Dalton's theory guided the pioneers of modern atomic theory to perform their experiments in search of the atom and its properties.

Chapter 7: The Structure of the Atom

Discovery of the Electron

Ionization of Gases, and Early Observations on Charged Rays

In the late 1800's, with William Crookes and Johann Hittorf's the invention of the Crookes-Hittorf tube, scientists became capable of observing two charges in the atom by ionizing gases.
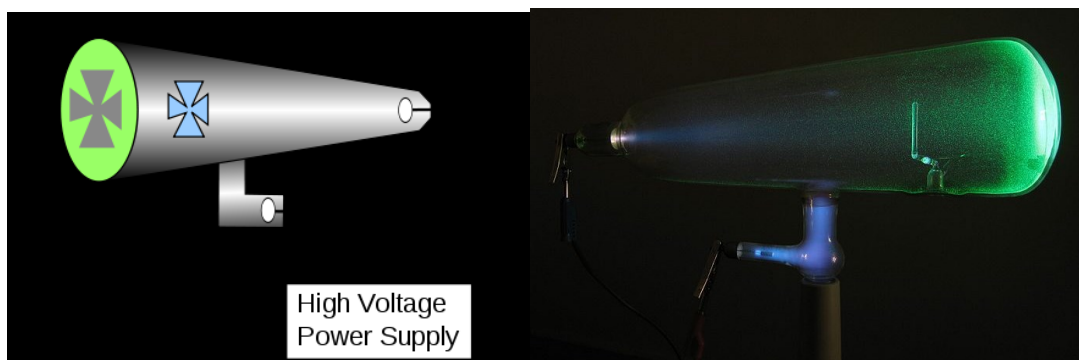
Figure 7.2. A diagram of the Crookes tube. The phosphor painted onto the end of the tube lights up when it is hit and excited by cathode rays, because the phosphor emits the energy that it gains from the electrons as visible light.

In 1869, Johann Hittorf discovered the cathode ray (negatively charged ray of electron), which was named by Eugen Goldstein. In 1886, Eugen Goldstein also discovered positively charged ions from the electric ionization of gases, which he called canal rays (positively charged anode rays). However, the positively charged ions all had different charge to mass ratios, depending on what gas was ionized. Charge to mass ratio is the charge density of a particle or ion, and a consistent charge to mass ratio may indicate the discovery of a particle. What Eugene Goldstein observed were positively charged ions, which were atoms with some electrons removed. However, the atom contains positively and negatively charged particles, along with the neutral neutron. The positively charged particles are too tightly bound with the neutrons in the nucleus to be separated. Thus, Goldstein's discovery of canal (anode) rays did not lead to the discovery of a subatomic particle, because the neutrons created inconsistencies in the mass to charge ratio of the nuclei of different atoms.

Chapter 7: The Structure of the Atom
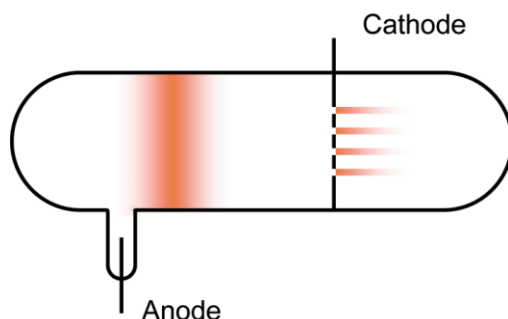
Figure 7.3. A diagram of canal (anode) rays, that Eugene Goldstein observed.

If there were only protons in the nucleus, then the charge to mass ratio would be constant, and Goldstein would have discovered the proton. Also, if he tried to determine the mass to charge ratio of the other ray (the cathode ray), he would have discovered the electron. However, this sets up Thomson to discover the electron, Mosley to discover the proton, and eventually, led to Chadwick's discovery of the neutron.

Cathode Rays

Out of the three atomic particles, the electron was discovered first. Englishman Sir J. J. Thomson discovered it in 1897, with a cathode ray generated in a Crookes tube. Previously, there had been speculation on the nature of what the cathode ray was. Heinrich Hertz had already done a similar experiment in 1893, and wrongly concluded that the cathode rays are unaffected by electric fields. Hertz also stated that the probability that the cathode rays are particles is very low, as he observed the cathode rays pass through gold film. According to Hertz, particles cannot pass through solid matter. After some thought, what Hertz said was illogical, because we frequently observe bullets passing through solid objects, and cathode rays are a lot faster than bullets, often having a velocity of 1/10th the speed of light!

Chapter 7: The Structure of the Atom
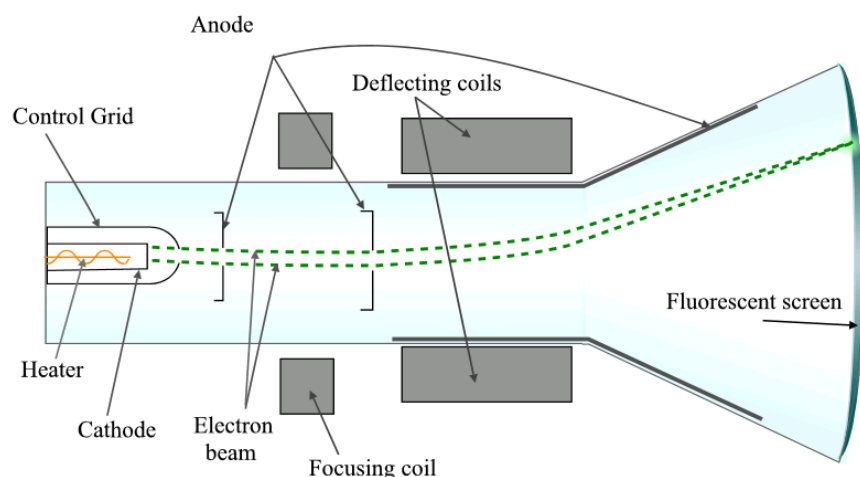
Figure 7.4. A diagram of J. J. Thomson's experimental setup.

Two years after Hertz, in 1895, Jean-Baptiste Perrin did a similar experiment, in which he observed that the cathode rays might be charged. Another two years later, in 1897, J. J. Thomson performed the same experiment as Hertz, to check the validity of Hertz's conclusions. Upon applying an electric field with two metal plates to the cathode ray, he found that the ray bent towards the positive plate!
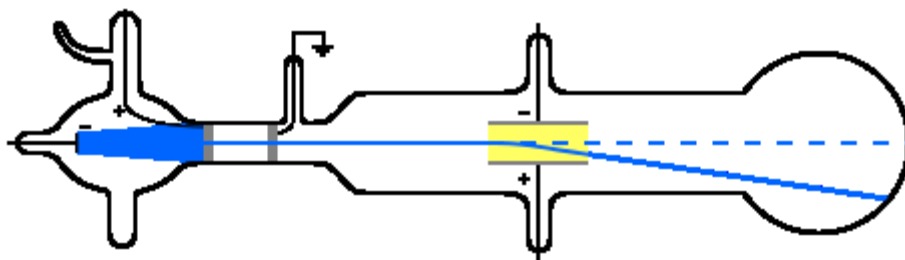
Figure 7.5. A diagram of what J. J. Thomson observed. The cathode ray, a beam of negatively charged electrons, bent towards the positive plate when the electric field is applied.

Hertz was wrong because his tube was a primitive version of what Thomson had. The tube was not completely evacuated, which led to the ionization of the remaining air. The ionized gas migrated towards both the positive and the negative plates, which masked the curvature of the cathode ray towards the positive plate. Hertz's conclusion accurately represents what he observed, but there was an error due to his crude equipment. Since Thomson was an early

Chapter 7: The Structure of the Atom

supporter of the particle theory of cathode rays, he concluded based upon his observations that there are particles much less massive than atoms, and by varying the electric field that he applied he calculated that the particles have a very large charge to mass ratio of 1.759×10^{11} C/kg. The modern accepted value for the charge to mass ratio of the electron is 1.7588196×10^{11} C/kg .

Measuring the Mass and Charge of the Electron

In 1909, Robert A. Millikan and his student, Harvey Fletcher, set out to measure the charge of the electron. Working at the University of Chicago, they performed the oil drop experiment. The oil drop experiment apparatus consisted of an atomizer, an electric field established by two plates that were positively charged and negatively charged, an ionizing radiation source (x-rays), and some oil. The atomizer sprayed the oil out from a nozzle, which produced uniform, very fine oil droplets. Then, the ionizing radiation ionized the oil droplets, giving the droplets some charge. Using the electric field, the oil drops could then be suspended when the electric force equaled the force on the oil drops due to gravity, thus allowing for him to detect multiples of the electric charge of the electron.
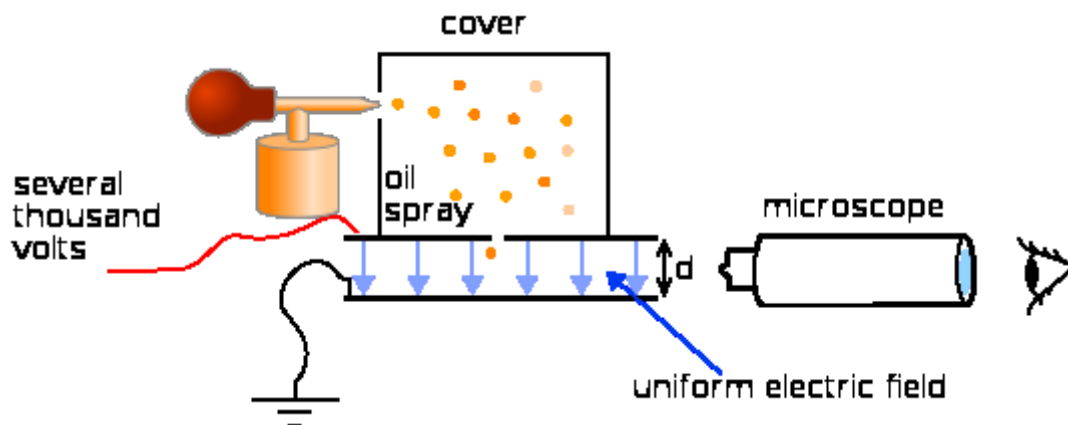
Figure 7.6. A diagram of the Millikan's oil drop experiment. Applying an electric field allows for the charged oil droplets to be suspended in air, allowing for the detection of multiples of the electronic charge, thus allowing for him to calculate the electronic charge.

Millikan found an excellent example of quantization, which led to his ability to find a value for the charge of the electron. He found that the charge the oil drops carried were all multiples of about 1.5924×10^{-19} C, which is not far from the current accepted value, which is

Chapter 7: The Structure of the Atom

1.602 176 62x10^{-19} C. He had an error of about 0.6%, which is very accurate given the instruments available at the time. Thus, he confirmed Thomson's hypothesis that the electron was a particle, and proceeded to conclude that the electron had a fixed charge, which we know of today as the elementary charge, *e*. Using the elementary charge, and the charge to mass ratio that J. J. Thomson determined earlier, he could calculate the mass of the electron, which he calculated to be approximately 9.05x10^{-31} kg. His result is very close to the modern accepted value of 9.109 383 56 $\times$ 10^{-31} kg.

Early Models of the Atom

The Plum Pudding Model

In 1904, J. J. Thomson proposed his plum-pudding model of the atom. He named it after an English food. In his model, the positive charge is distributed through space, and the negative charge is embodied in "corpuscles," which are scattered uniformly in the positive charge. Since elements and compounds are neutral, there must be some positive component to the atom, leading to his conclusion that there is some positive substance that embodies the negatively charged electrons.
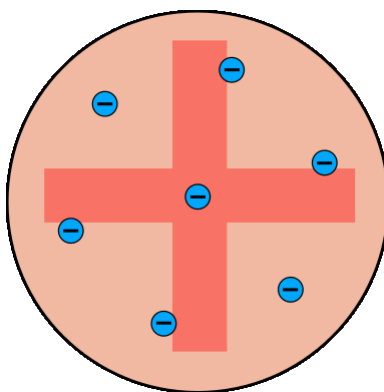
Figure 7.7. A diagram of J. J. Thomson's plum pudding model. The negatively charged "corpuscles" are embedded in a larger positive charge.

The Saturnian Model

One major opponent of the plum-pudding model was Hantaro Nagaoka, who proposed the Saturnian model in 1904. In his model, the electrons revolve around the positively charged

Chapter 7: The Structure of the Atom

center of the atom. Nagaoka thought that it was unlikely that opposite charges can penetrate each other and exist in the same space. Nagaoka proceeded to propose his model of the atom, which involves the electrons circulating around a positively charged center like how the ice rings of Saturn revolve around the planet. Based upon his model, he correctly predicted that the atom has a massive positive center, not much unlike the idea of the nucleus, and that electrons revolve around the nucleus due to electrostatic attraction. Although many of his other predictions were incorrect, both mentioned above were correct, and are indeed similar to the characteristics of Saturn, a similar system. Both have significant centers, and both are held together by inverse square forces. Saturn has a very high mass, and the nucleus has a high charge. Saturn is held together by gravity, and the atom is held together by electrostatic attractions.

Inverse Square Forces

Inverse square forces are forces that follow the corresponding relation: $F \propto \frac{1}{r^2}$ (the force is proportional to the inverse square of the distance between the two objects that are affected by the force). The most common inverse square forces that we encounter are the force due to gravity, and the electrostatic force. Inverse square forces are frequently associated with orbits.

Newtonian Equation for Approximating the Force of Gravity

The force due to gravity is approximately $F_g = \frac{Gm_1m_2}{r^2}$. The potential energy due to the force of gravity is approximately equal to $U_g = -\frac{Gm_1m_2}{r}$, where G is a constant, m_1 and m_2 are the two objects with mass, and r is the separation between the two masses. This is not exact, but nevertheless is a very close approximation.

Coulomb's Law for Electrostatic Interactions

The electrostatic force is equal to $F_{el} = \frac{kq_1q_2}{r^2}$. The potential energy due to the electrostatic force is equal to $U_{el} = -\frac{kq_1q_2}{r}$, where k is a constant called Coulomb's constant,

Chapter 7: The Structure of the Atom

which is equal to $k = \frac{1}{4\pi\epsilon_0} = 8.98 \times 10^9 \frac{\text{Nm}^2}{\text{C}^2}$, q_1 and q_2 are the two charges in coulombs, and r being the separation between the two charges. This is exact, as we do not know of any deviation from Coulomb's law.
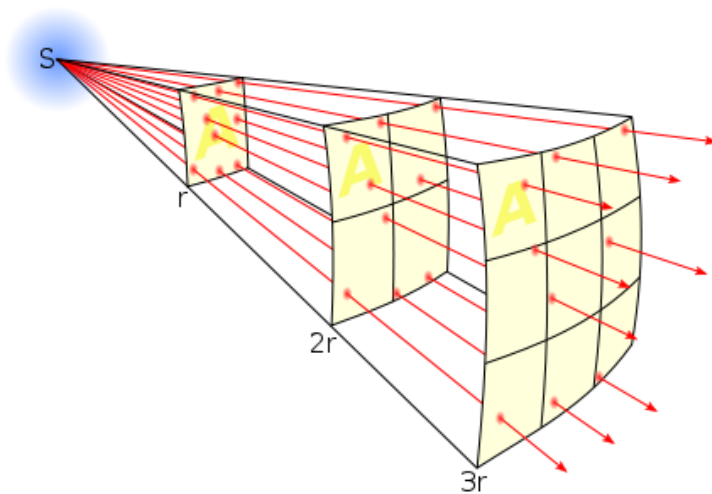
Figure 7.8. A diagram of an inverse square law. When distance is doubled, the effect is fourthed, and when distance is tripled, the effect is ninthed. In general, when the distance is multiplied by n, the effect of the force is divided by n^2.
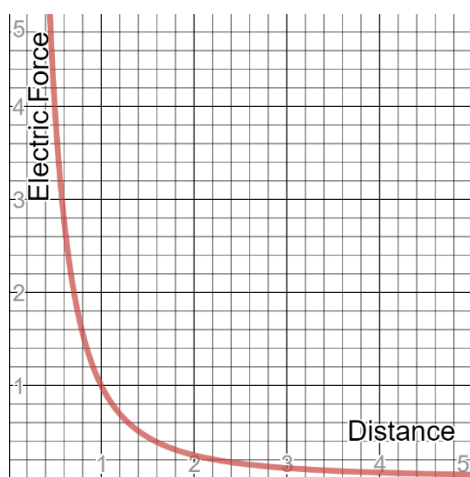
Figure 7.9. An inverse square force versus distance graph.

Chapter 7: The Structure of the Atom

The Nuclear Atom and The Gold Foil Experiment

Between 1908 and 1913, two students of Ernest Rutherford performed a series of experiments, known as the Rutherford gold foil experiment. Hans Geiger and Ernest Marsden shot alpha particles at foils of various metals (gold, aluminium, etc.), and observed where particles struck a fluorescent screen. The alpha particles were from the radioactive decay of a sample of radium. An alpha particle is the nucleus of a helium atom, with two neutrons and two protons. Therefore, it has a 2+ positive charge, and would be repelled strongly by the protons in an atom.
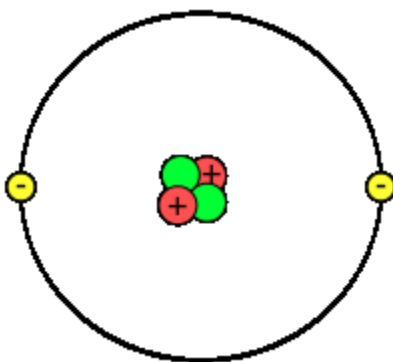
Figure 7.10. A simplified diagram of a helium-4 atom, which has two electrons, two neutrons, and two protons.

Chapter 7: The Structure of the Atom
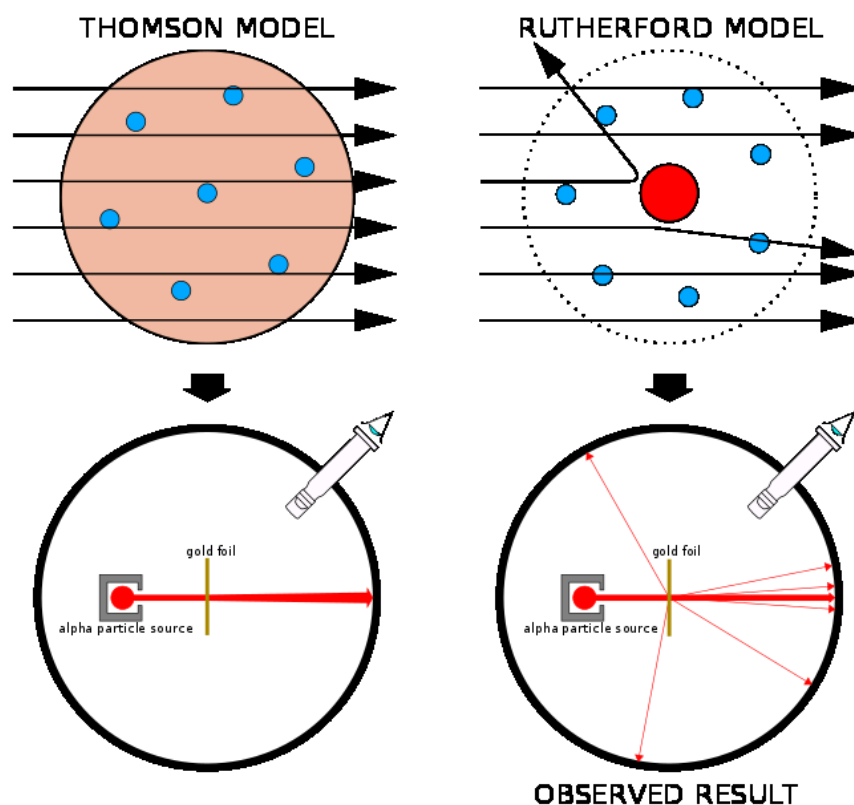
Figure 7.11. A diagram of the Geiger Marsden Experiment. The left illustrates what would have happened if the positive charge was distributed evenly throughout the atom. However, the observed results of the experiment proved that the positive charge was concentrated in the center, in the nucleus of the atom.

During the experiment, nearly all the particles passed through without significant deflection. However, about one out of 8000 alpha particles was reflected almost directly backwards. In the words of Rutherford, "it was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you." This meant that the atom is almost completely empty space, with all the positive charge concentrated in the center, and the negative charge distributed nearly evenly in space.

In a sense, J. J. Thomson was right, that one charge is distributed in space, while the other is concentrated in "corpuscles." However, he got the charges wrong! Modern physics supports the notion that electrons are distributed in space as waves. J. J. Thomson's son, G. P. Thomson, proved that electrons are waves by conducting a series of diffraction experiments. We only represent electrons as distinct particles, so that we can understand reactions easier! Also, we call his corpuscle a nucleus instead. Rutherford proposed the Rutherford model, sometimes called the

Chapter 7: The Structure of the Atom

planetary model, which included the idea of the nuclear atom in 1911. Some say that he stole the credit from Geiger and Marsden, because most classes only mention Rutherford!

Discovery of the Proton, and the Modern Periodic Table

The van den Broek Hypothesis

In July 1911, one month after Rutherford's publication, Antonius van den Broek proposed a relationship between the atomic number according to the element's location on the periodic table, and the charge of the nucleus. Although Rutherford determined that there was a small, dense, highly charged nucleus somewhere in the atom, Rutherford failed to explain the relationship between atomic mass, atomic number, electron number, and nuclear charge. Rutherford initially proposed that the nucleus might be made up of helium nuclei, with the helium nucleus of two protons and two neutrons as the fundamental unit of the nucleus. However, observations of atomic mass and atomic number did not support that initial hypothesis, because there are numerous elements which do not have a mass number equal to two times their atomic number, and elements with odd mass numbers. Van den Broek first observed the correlation, and proposed that the nuclear charge is equal to the atomic number. This necessitates the existence of some entity with a positive charge. Since the amount of positive charge must equal the amount of negative charge to make atoms neutral, this also indicated that whatever entity that possesses the positive charge has a charge of the same magnitude as the electronic charge. Indeed, in a neutral atom, the number of electrons is equal to the number of protons, which is in turn equal to the atomic number of the element that the atom belongs to.

Mosley's Experiment

In 1913, a student of Rutherford named Henry Mosley, shot x-rays through crystals of various elements. Most of the crystal targets that the x-rays were shot at were metals. In one of the first significant applications of Bragg's law of diffraction, he determined the x-ray spectra wavelengths, and observed that there was a mathematical relationship between the frequency, and the atomic numbers on the periodic table. With the pattern that he found in the frequencies, he could order most of the elements mostly by the atomic numbers they were previously assigned. Borrowing the concept of the nuclear atom from Rutherford, and the concept that the

Chapter 7: The Structure of the Atom

nuclear charge is equal to the atomic number, he concluded that the x-ray spectra were related to the positive charge of the nucleus, rather than atomic mass. He was considered a pioneer of x-ray spectroscopy, the predecessor of x-ray crystallography, and the pattern he found relating frequency and atomic number was named Mosley's law in his honor.
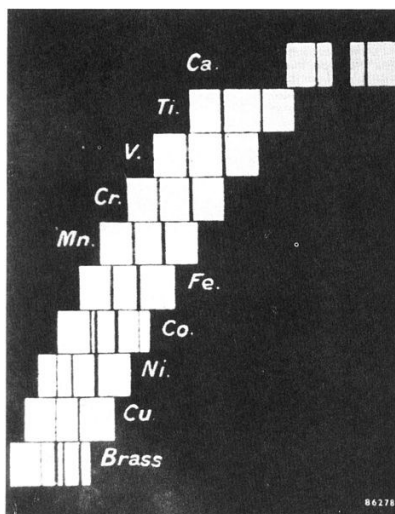
Figure 7.12. A picture of Mosley's results, that allowed for him to correlate proton number and atomic number.

Mosley had discovered the proton, and established that the number of protons is equal to the atomic number of the element. This set forth the modern periodic table, which represented the elements far better than Mendeleev and Meyer's previous periodic table that was organized by atomic mass. His conclusion is consistent with both the work of his mentor, and van den Broek, and as of now, we accept the atomic number to be the number of protons in the nucleus, and to represent the charge of the nucleus. Mosley's results also clarified previous ambiguities, such as where cobalt and nickel belonged (because they have approximately the same atomic mass), and created a set order of where the elements should be placed, based upon a well-defined physical property, which is the number of protons. This organized the elements well based upon their reactivity and characteristics, because the charge of the nucleus determines how many electrons are in a neutral atom, and thus determines many of the chemical properties of the element. Sadly, he died in World War I, and that resulted in England's ban on the enlistment of prominent scientists in the military. If he had lived, he would have done much more, and perhaps surpass his mentor.

Chapter 7: The Structure of the Atom

Rutherford Splitting the Atom

Rutherford confirmed the existence of the proton in 1919, when he "split the atom." Rutherford knew of alpha and beta particles released in radioactive decay along with the gamma ray since 1898, and he was the one who found that atoms undergoing nuclear reactions release two types of particles, one type with the mass of an electron, which can either be an electron or the electron's positively charged antiparticle, the positron, which he called the beta particle, and the other type, with the mass of a helium-4 nucleus, which indeed turned out to be a helium-4 nucleus with two protons and two neutrons, which he called the alpha particle. The last type of radiation, the gamma ray, was simply a very energetic form of electromagnetic radiation.
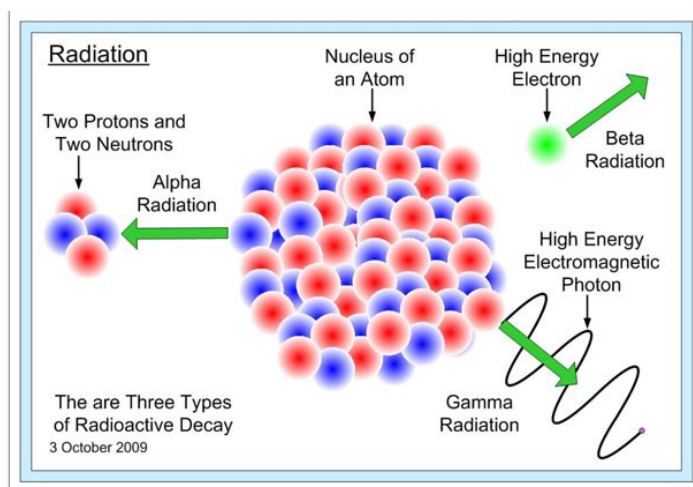
Figure 7.13. The three types of radiation known to Rutherford, before the discovery of neutron rays.

When he split the atom in 1919, he bombarded nitrogen-14 with alpha particles, which formed oxygen-17 and resulted in the emission of the proton. The nitrogen-14 captured the alpha particle and simultaneously released the proton, going from a mass number of 14+4-1=17 and an atomic number of 7+2-1=8, thus producing oxygen-17.

Something Doesn't Add Up

However, there is still one anomality. Because the atomic masses are not completely in accordance to the atomic numbers, there is very likely another subatomic particle that bears no

Chapter 7: The Structure of the Atom

charge that has not been discovered yet. This neutral particle was not found until the model of the atom was nearly complete.

Waves

Measurements of Waves
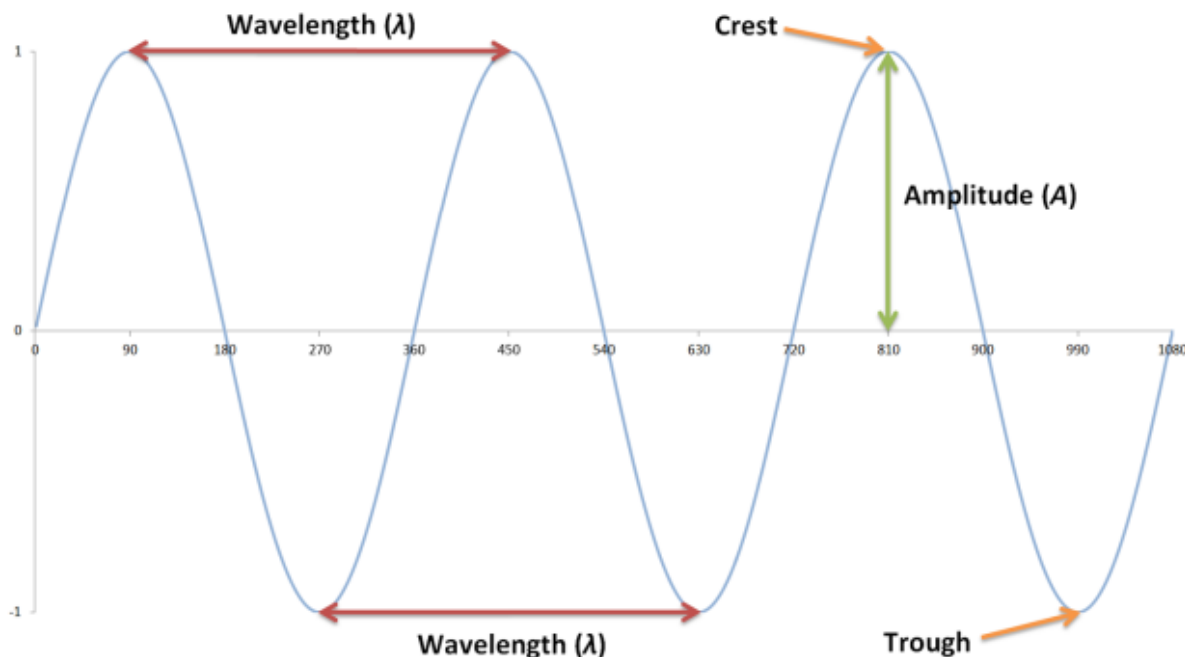
Figure 7.14. A diagram of the features of a transverse wave. The wavelength, λ, crests, troughs, and the amplitude, A, are labeled. The frequency is the number of wavelengths that pass during a single second.

Waves are periodic changes through space, meaning that there is a pattern that repeats itself. The most familiar examples are light and sound. Waves are generally measured using four values. The first is the wavelength, λ, or how long is one cycle of the wave in metres. The second is the frequency, v, or how many cycles of oscillation occur in 1 second. The third, is the speed of propagation, or how fast does the wave travel through a medium, and for electromagnetic radiation in a vacuum, the speed of propagation is the speed of light, $c = 2.99 * 10^8 \frac{m}{s}$. A medium is anything that the wave is travelling through, whether it be air or empty space. The

Chapter 7: The Structure of the Atom

fourth is amplitude, *A*, or how intense is the wave. Waves may be either transverse or longitudinal, or a mixture of the two.

Wavelength, represented by λ, is in metres. Frequency, represented by ν, has units of inverse seconds, also known as hertz (Hz=s^{-1}). Speed of propagation, represented by c, has units of meters per second. Since the wavelength, frequency, and speed of propagation represent the same wave, multiplying wavelength by frequency yields the speed of propagation in meters/second. It makes sense that multiplying a distance, by how many of those distances are traveled in a second, yields the total distance traveled in a second.

$$\left(\frac{m}{s}\right) = (m)\left(\frac{1}{s}\right) \rightarrow c = \lambda\nu$$
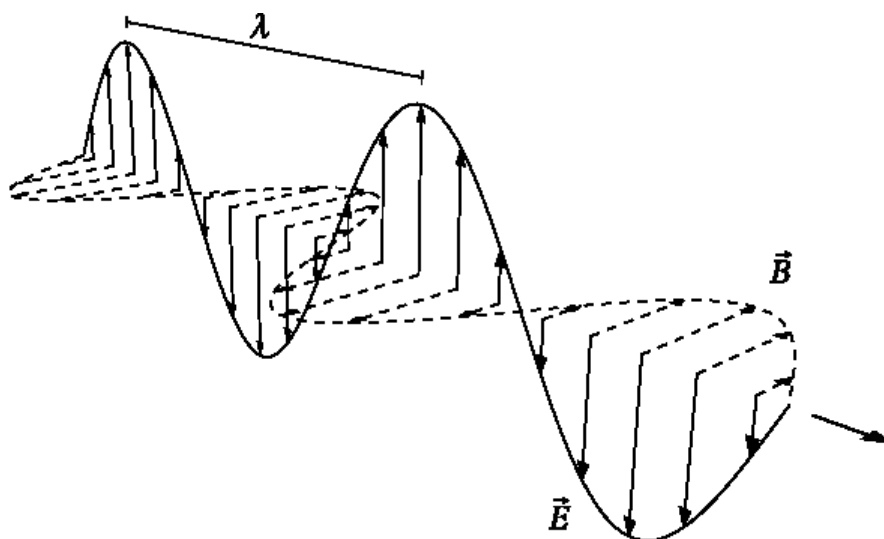
Figure 7.15. A labeled diagram of electromagnetic radiation. $\vec{E}$ is the electric field and $\vec{B}$ is the magnetic field. The two are orthogonal (perpendicular) to each other, and are said to be 90 degrees out of phase, because the electric field is at a max when the electric field is at a min, and vice versa. The arrow indicates the direction of propagation. The frequency is the number of oscillations that pass a fixed point in a single second.

Amplitude and the Principle of Superposition

The amplitude, *A*, is measured in meters, and it is usually represented as the height of the wave from the mid-line to an extreme. The peaks are known as crests, and the minimums are known as troughs. The amplitude depends on how strong a single wave is, and where the wave is located relative to other waves. The stronger a single wave is, the larger the amplitude is. When we have waves occupying the same space, they add. This is called the principle of superposition.

Chapter 7: The Structure of the Atom

The principle of superposition says that to get the total effect at a single point due to one or more waves, what you do is add the waves together, because the effect due to interference between the two waves is the same as if you calculate the effect of each wave and sum up the two effects.

Interference

That leads us to constructive and destructive interference. Constructive interference occurs when waves are the same sign, or phase, at a given location. The waves are working together to produce a stronger effect, as shown by the greater amplitude of the resulting, equivalent wave. However, destructive interference is the complete opposite, where two waves are completely out of phase, and cancel each other out.
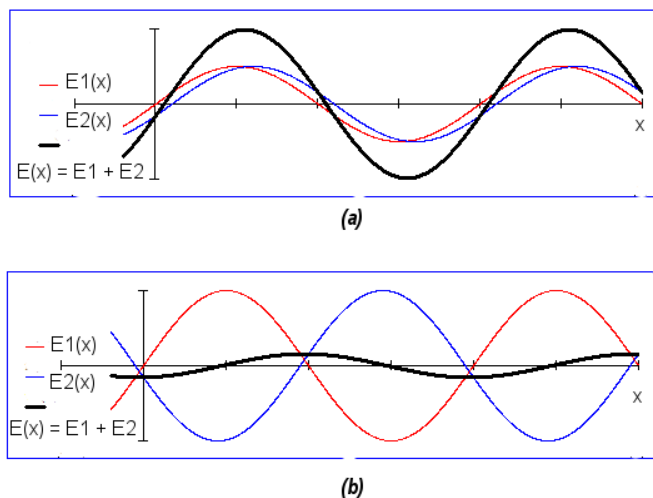
Figure 7.16. According to the principle of superposition, the result of two waves can be obtained by adding them together. Thus, constructive interference is shown above (a), and destructive interference is shown below (b).

Complete destructive interference results in no effect in the space that the two waves occupy. Constructive interference is sometimes called resonance, and destructive interference is sometimes called dissonance. Constructive interference occurs whenever anyone plays an instrument. Destructive interference is used in noise-canceling devices. Noise-canceling devices detect a wave, invert it, and produce the inverted wave. According to the principle of

Chapter 7: The Structure of the Atom

superposition, adding the inverted wave to the original noise wave generates a net effect of 0, thus reducing or eliminating the annoying sound.

Characteristics of Light

Evidence of the Wave Nature of Light: Diffraction

The nature of light puzzled scientists for hundreds of years. When Newton published his *Opticks* in 1704, he popularized the idea that white light is made up of many colors. Thus, many saw light as a continuum of waves with different wavelengths. This wave-like nature of light was supported by the diffraction of light. Diffraction is a characteristic of waves. When something passes through a narrow aperture and spreads out, it has undergone diffraction. When light is shined through diffraction grating, as in Young's double-slit experiment in 1801, the light indeed diffracts, which is evidence that supports the idea that light is composed of waves.
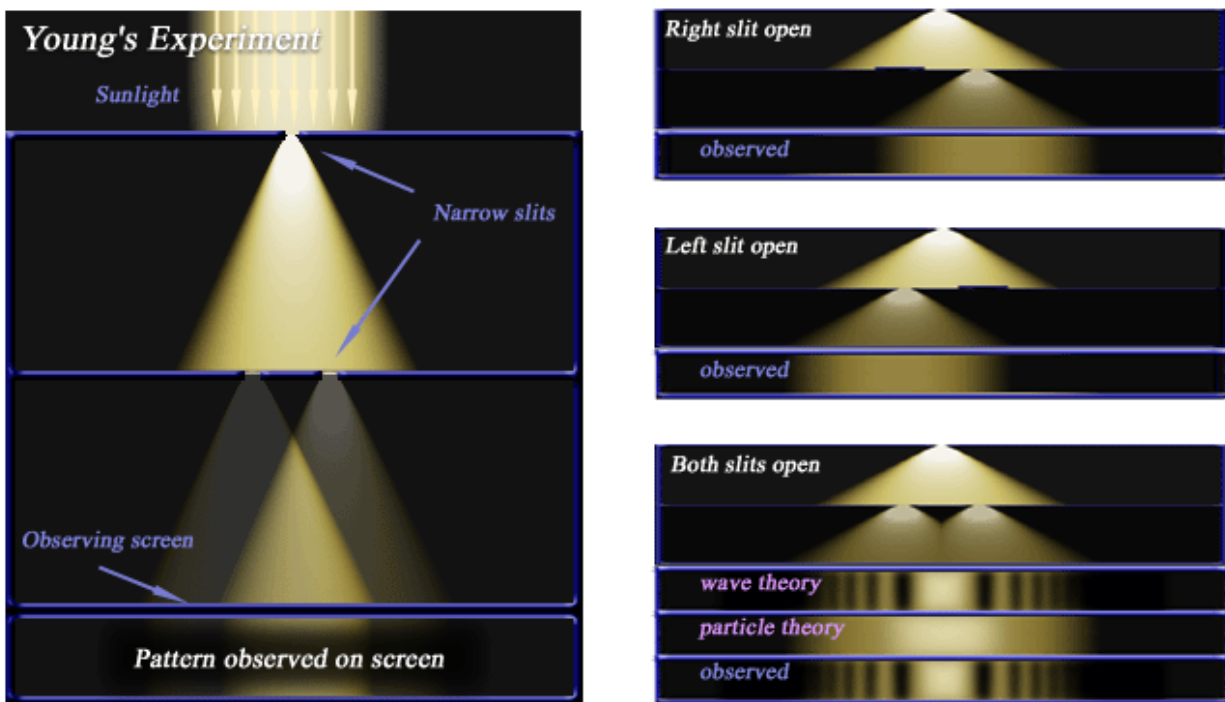
Figure 7.17. Young's double slit experiment is evidence of the wave properties of light. Waves are known to undergo diffraction, as observed in the patterns resulting from the experiment.

Chapter 7: The Structure of the Atom

Evidence of the Particle Nature of Light: The Photoelectric Effect

In 1887, Heinrich Hertz observed that when light struck a metallic surface, electrons were displaced. What he observed is now known as the photoelectric effect. The photoelectric effect is evidence of the particle nature of light, and caused some amount of discomfort in the scientific community because particles were seen to be distinct from waves. In 1900, a major revolution hit the scientific community. Max Planck proposed the Planck postulate along with his law for black body radiation, the Planck law. Planck, known as the father of quantization, proposed his idea that certain quantities are made up of small fundamental units that cannot be made smaller. Thus, Planck set forth the theory that there is a smallest quantity that can exist for anything. The Planck-Einstein relation is one of the fundamental ideas of quantum physics, that energy transferred as light may only be transferred in set amounts at a time. It relates the energy of a photon to the wavelength and frequency of the photon.

Planck-Einstein Relation: $E_{photon} = h\nu$, where h is planck's constant $\approx 6.626 * 10^{-34}$ J $*$ s

Equivalently, because $c = \lambda\nu$ then $\nu = \frac{c}{\lambda}$ and $E_{photon} = h\nu = \frac{hc}{\lambda}$
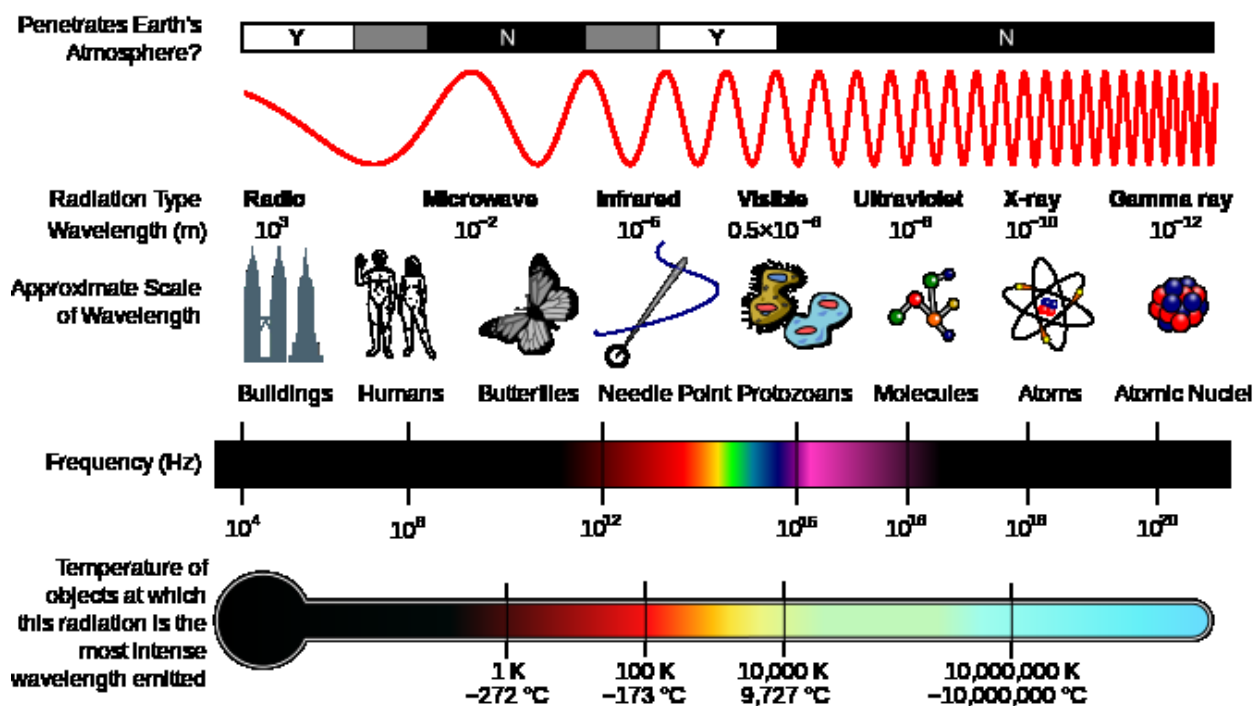
Figure 7.18. The electromagnetic spectrum.

Chapter 7: The Structure of the Atom

Thus, if the photon is seen as the fundamental "packet" of energy, the amount of energy transferred by light only occurs in multiples of the energy of the photon.

$$E_{\text{transferred}} = \text{n}h\nu = \frac{\text{n}hc}{\lambda}, \text{ where n is an integer.}$$

In 1905, Albert Einstein explained the photoelectric effect in his Nobel-Prize winning annus mirabilis paper "On a Heuristic Viewpoint Concerning the Production and Transformation of Light." He explained that the energies electrons could have are distinct, and that photons can carry energy to excite the electrons from one energy level to a higher energy level. In an atom, there are many states of energy which are allowed, but the energies are not continuous. According to what Planck proposed, energy is quantized. The minimum energy to excite an electron out of a solid (ex: piece of metal, glass, etc.) is the work function, Φ. Thus, only photons carrying that minimum required energy can excite the electron out of a solid. The remaining energy is given to the electron as kinetic energy. Thus, only photons above a certain minimum threshold frequency, and below a maximum wavelength, can excite an electron out of a solid.

$$\Delta E_{\text{Kinetic energy of electron}} = E_{\text{photon}} - \Phi$$

When the electron is again captured by what emitted it, the electron emits the energy back as a photon. For atoms, a similar effect is observed when photons excite electrons from one energy level to another, and when electrons go from a higher to lower energy level, and release the energy previously absorbed as a photon. Therefore, this supports that the energy levels in an atom are quantized, and the collision that needs to take place between a photon and an electron as observed by Heinrich Hertz as the photoelectric effect is evidence of the particle nature of light. Thus, this also explains why there are dark absorption lines in sunlight that correspond to the wavelengths at which electrons in certain elements are excited. These so-called "Fraunhofer lines" were observed in 1802 by William Hyde Wollaston, and named after Joseph von Fraunhofer, who rediscovered the lines in 1814. In 1859, Kirchhoff and Bunsen correlated these lines to the emission lines of certain elements when they were heated in a flame test, indicating that those very same elements were the ones that captured the light of certain frequencies.

Chapter 7: The Structure of the Atom
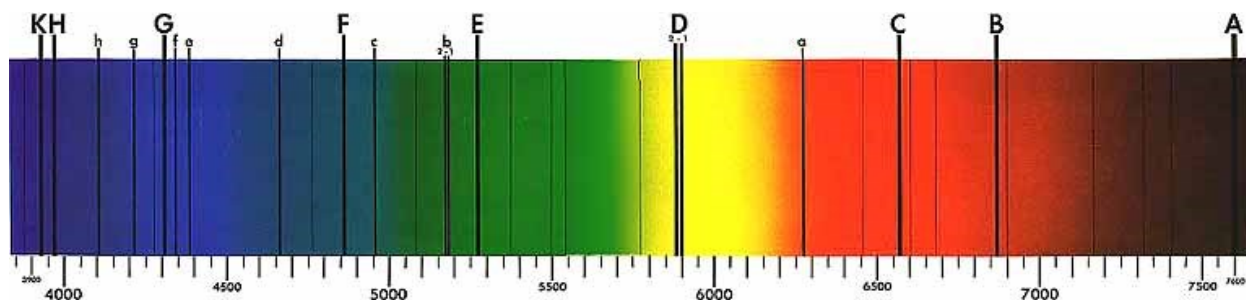
Figure 7.19. Dark-line spectra, similar to the ones observed by Fraunhofer, which result from the absorption of certain wavelengths of light. The fixed wavelengths are evidence that supports quantization. The numbers underneath are wavelengths in angstroms ($1 \text{ Å} = 10^{-10}$ m). Fraunhofer labeled the absorption spectrum wavelengths of Sodium from A through K. The absorption spectrum shown above is for Na, and features the prominent strong doublet "D-lines," at 5890 Å and 5896 Å. Because absorption is the reverse of emission, and the same amount of energy is emitted as absorbed according to the conservation of energy, the bright-line spectra created by the emission of light by Sodium is complementary to its dark-line spectra. Thus, in the emission spectra, the colored areas would appear black, and the black lines would appear to be colored. Putting the two spectra together generates a complete spectrum, which includes light of all wavelengths.

Matter Waves, and Wave-Particle Duality

The de Broglie Hypothesis

In 1924, Louis de Broglie proposed that all matter had a corresponding wavelength. He hypothesized that any given body or particle is a matter wave. His equation describes the wavelength of a particle that has a certain amount of momentum.

De Broglie wave equation:

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

Where λ is the wavelength, $h = 6.626\,070\,040 \times 10^{-34}$ J $*$ s is Planck's constant, m is mass, v is velocity, and $mv=p$ is the linear momentum of the particle.

The Davisson Germer Experiment, and G. P. Thomson's Conclusion

In 1927, de Broglie's hypothesis was confirmed by the diffraction of electrons that were shot at metal foils in a series of experiments conducted by G. P. Thomson. At the same time, the Clinton Davisson and Lester Germer experiment occurred, and it was found that slow moving electrons were diffracted by nickel crystals.

Chapter 7: The Structure of the Atom
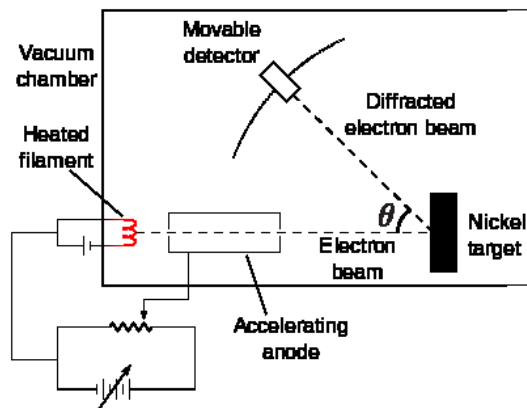
Figure 7.20. A diagram of the Davisson Germer experiment, where the diffraction of electrons revealed that electrons do indeed diffract. Diffraction was a characteristic that were previously only attributed to waves. The discovery led to the concept of wave-particle duality, that all matter can be represented as both particles and waves.

Modern double-slit experiments offer additional proof, when it was observed that light, ions, atoms, and molecules all undergo diffraction, a behavior classically reserved for waves. This supported a new idea, which is the wave-particle duality of matter, that everything has wave and particle characteristics. We only describe something as a particle or a wave to make it easier to understand. However, as de Broglie proposed, it is both a wave and a particle because waves and particles are just different ways to describe different behaviors of a single object. Following the logic of Planck, the wave-like characteristics of matter suggests that all matter may possibly be quantized. Even light, classically represented as a wave, can be represented as a particle with mass.

Hydrogen Emission Spectra

The Balmer Equation

Natural light is composed of a continuous spectrum, as demonstrated by Isaac Newton in the 1600's, when he separated the different frequencies and colors of light with prisms.

Chapter 7: The Structure of the Atom
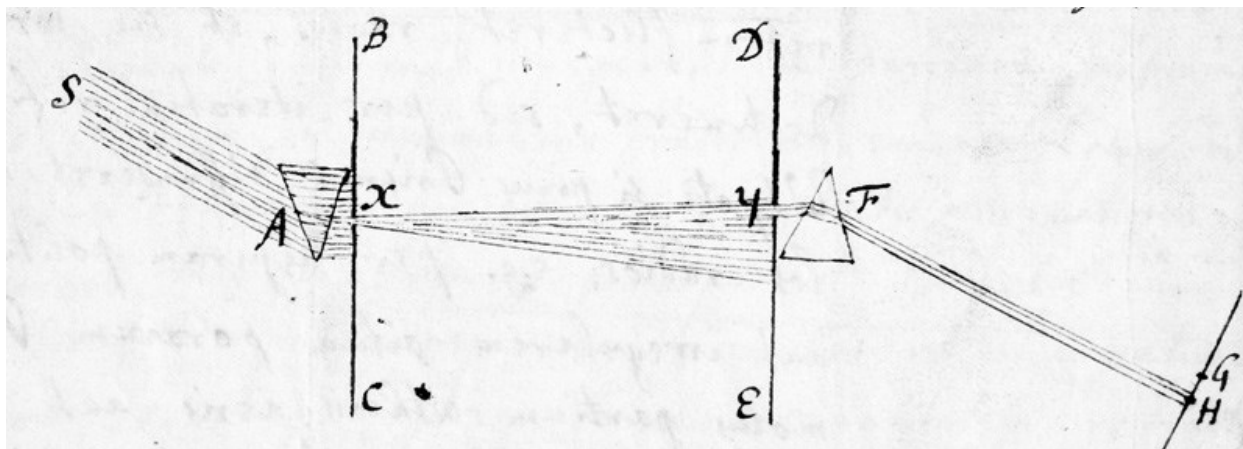
Figure 7.21. Newton's drawing of his experiment, in which he separated light using prisms into components with different frequencies, thus showing that white light was composed of a spectrum of colors, but each individual color was only light of a certain frequency.

However, you can only see the portion of the electromagnetic spectrum that is about 400 to 750 nanometers. Since the late 1800s, it was known that exciting the hydrogen atom led to the emission of distinct wavelengths of light. These spectra puzzled the people who observed them. Since visible light is most easily observed, it was observed first. In 1885, Johann Balmer observed that the wavelengths of the visible light followed the following rule, which is known as the Balmer formula. The visible emission spectra are named the Balmer series in his honor.

Balmer's Formula:

$$\lambda = B\left(\frac{n^2}{n^2 - m^2}\right)$$

Where λ is the wavelength, B is a constant equal to 3.6450682×10^{-7} meters, $m=2$, and n is an integer greater than m.

Other series have been observed, in which m is not equal to 2. For example, the Lyman series ($m=1$), Paschen series ($m=3$), etc, which are described by the Rydberg Equation.

The Rydberg Equation: Evidence of Quantization

In 1888, Johannes Rydberg presented his equation to explain the wavelengths of the emission spectra of the hydrogen atom. He found that the inverse of the wavelength, the wavenumber, was easier to relate to the emission spectra. He knew of Balmer's formula, and

Chapter 7: The Structure of the Atom

revised it. Not only did Rydberg's formula fit the Balmer series (*m*=2, visible radiation), it also worked for other series as well, such as the Paschen series (*m*=3, infrared radiation), and the Lyman series (*m*=1, ultraviolet radiation). When *m*=2, the Rydberg formula is the Balmer formula, only rearranged. However, note that there are only discrete values in the emission spectra. The emission spectra suggested that the energy emitted is quantized, and supports Planck's idea of quantization, because the quantization of the emitted energy indicates that the hydrogen electron may only have discrete energies.
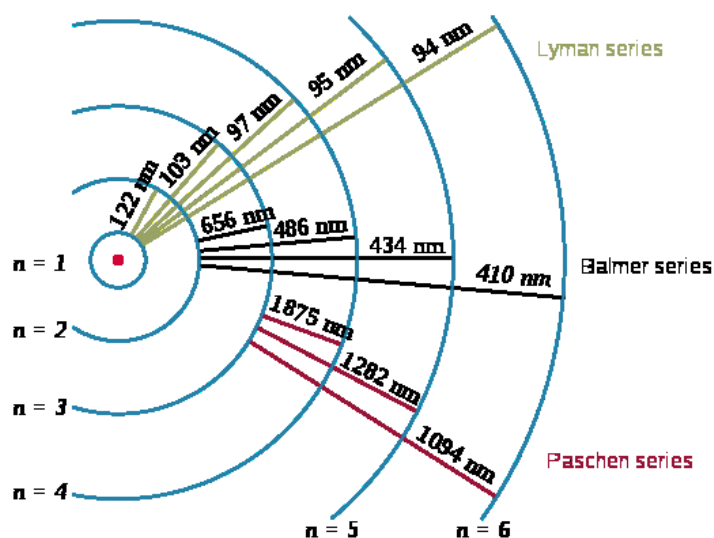
Figure 7.22. The Lyman, Balmer, and Paschen series, the initial and final energy levels of the electron for a hydrogen atom, and the wavelengths that are emitted.

Rydberg proposed the following formula to explain all the emission spectra of the hydrogen atom.

Rydberg's Equation:
$$\frac{1}{\lambda} = \frac{4}{B}\left(\frac{1}{m^2} - \frac{1}{n^2}\right) = R_\text{H}\left(\frac{1}{m^2} - \frac{1}{n^2}\right) = R_\text{H}\left(\frac{n^2 - m^2}{m^2 n^2}\right)$$

Where $\frac{1}{\lambda}$ is the wave number, both *m* and *n* are integers with *n* being greater than *m*, and R_H is the Rydberg constant for the hydrogen atom, which is equal to 4 divided by Balmer's constant.

Chapter 7: The Structure of the Atom

Finding the Change in Energy of a Hydrogen Electron

Using this formula, we can find the wavelength, frequency, and energy of the photon emitted, along with the change in energy of the hydrogen atom as it emits the photon.

$$c = \lambda v \rightarrow c\left(\frac{1}{\lambda}\right) = v$$

$$E_{\text{photon}} = hv = hc\left(\frac{1}{\lambda}\right)$$

$E_{\text{photon}} = -\Delta E_{\text{H atom}}$, because the hydrogen atom loses the energy emitted as the photon.

Thus, a hydrogen electron can only emit photons of certain wavelengths. Likewise, when a hydrogen atom absorbs energy to excite the electron to higher energy levels, the photon must have a minimum amount of energy (thus a maximum wavelength, and a minimum frequency), which corresponds to the amount of energy that is emitted by the opposite electronic transition.

Mass of Light

Given the equivalence of mass and energy, we find that light particles are supposed to have mass, and thus, push the object that it strikes. The mass can be found as follows:

$$E = hv$$

$$E = mc^2$$

$$hv = mc^2$$

$$\frac{hv}{c^2} = m$$

Although the photon does not have mass when it is as rest (a photon has no energy, and does not exist when it is as rest), when it is travelling at the speed of light, and has a certain frequency or wavelength, the photon indeed does have a small amount of mass. This can also be observed during nuclear decay, because mass is lost as gamma rays, and when light bends around massive objects such as black holes, because gravity acts on objects that have mass. In a more modern application, we see that when radiation hits an object, the object experiences a force. This "radiation pressure," which is the principle behind solar sails, also confirms that light has mass.

Chapter 7: The Structure of the Atom

The Rutherford-Bohr Model: A Quantum Representation of the Atom

Based upon the idea of quantization set forth by Planck, the emission spectra of the hydrogen atom, and the concept of the nuclear atom, Niels Bohr and Ernest Rutherford proposed their own model of the atom. This became known as the Rutherford-Bohr model. They already knew that the electrons surrounded the nucleus, but did not know how. The previously proposed solar-system-like models did not work, because the electrons would repel each other, lose energy, and eventually spiral and crash into the nucleus. Thus, instead of considering all motions that classical mechanics permits, Bohr in 1913 proposed that maybe only certain motions are allowed, and that the atoms are restricted to only a few interactions that are allowed by classical mechanics. Thus, he eventually quantized the atom by imposing the following rules on electron interactions in his model of the atom.

Bohr's Theory Included:
1. Electrons orbit the nucleus in fixed orbits, called stationary orbits
2. These orbits are at a set distance from the nucleus, and each orbit has a distinct energy, called a shell. This quantized the orbits of the electron.
3. In these stationary orbits, the electrons undergo uniform circular motion, thus the acceleration due to the electrostatic attraction between the nucleus and the atom does not result in a change of energy. This effectively sets the energy of the electron at a constant.
4. The electrons can absorb and emit set quantities of energy, and thus move from orbit to orbit. Therefore, the atom's energy levels are quantized. However, Bohr did not believe in the existence of photons, which are quantized according to the Planck-Einstein postulate.

The Rutherford-Bohr model correctly predicted the Rydberg emissions of the hydrogen atom, and the radius at which the electron in a hydrogen atom is most likely to be found, thus providing support for quantization. His Bohr radius is about 0.53 Å, with an angstrom, Å, being equal to 10^{-10} m. However, Bohr was not able to calculate anything for an atom with more than one electron, because repulsion between electrons makes exact values for systems with more than one electron impossible to calculate.

Chapter 7: The Structure of the Atom
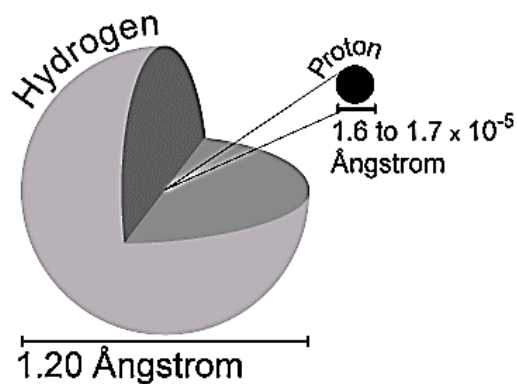
Figure 7.23. The relative size of the hydrogen atom. Note how small the proton is, relative to the size of the atom (**1 Å = 10^{-10} m**).

The Beginnings of a New Mechanics: The Schrodinger Equation

A Shift in Perspective

De Broglie reinterpreted the Rutherford-Bohr model in 1924, and proposed that the electrons were waves, thus beginning the era of wave mechanics. Thus, he proposed that the electrons in the Bohr atom were simply resonating at an average distance of 0.53 Å.
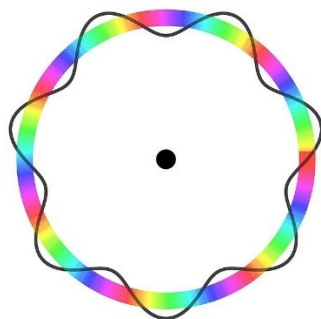
Figure 7.24. According to de Broglie, the electron is a standing wave, which is at an average radius of 0.53 angstroms from the center of the nucleus.

Wave mechanics is an important field which was later combined with quantum mechanics. In the 1920s, what became known as the Schrodinger wave equation was formulated. Schrodinger derived the equation in 1926. The equation was based upon the wave nature of electrons, and the concept of the quantum atom. A wavefunction describes how electrons reside and move within an atom. When Schrodinger formulated his equation, he showed that it was consistent with the spectral energies of hydrogen, and confirmed that the radius at which the

Chapter 7: The Structure of the Atom

hydrogen electron was most likely to be found was indeed the Bohr radius. Wavefunctions are represented by the Greek character Ψ.

The Heisenberg Uncertainty Principle, and the Observer Effect

With the introduction of wave functions, Werner Heisenberg proposed his Heisenberg uncertainty principle in 1927, which states that it is impossible to find both the position and momentum of a particle exactly. In fact, it is not even possible to calculate both accurately. The following inequality derived by Earle Hesse Kennard in 1927 means that the product of the standard deviation of position and momentum is greater than the Planck's constant divided by 4π. That just means that there is certainly uncertainty in our estimation of both of the quantities. The standard deviation is the average amount of error in the calculated value. Thus, the product of the error in the position and the error in the momentum of the particle is approximately $\frac{h}{4\pi}$. Momentum is defined as mass times velocity, and is written as $p = mv$.

Kennard's Inequality for the Heisenberg Uncertainty:
$$\sigma_x \sigma_p \geq \frac{h}{4\pi}$$

Sometimes, the inequality is also written as follows:
$$\sigma_x \sigma_p \geq \frac{\hbar}{2}, \text{where } \hbar, \text{the reduced Planck's constant, is equal to } \frac{h}{2\pi}$$

This type of relation occurs in all systems involving waves, and it is because of an inability to mathematically calculate two variables related in this manner to a greater degree of precision. The two variables, in this case being position and momentum, are complementary variables. In all wave-like systems, complementary variables cannot be simultaneously determined nor calculated precisely. The Heisenberg Uncertainty principle has been frequently accepted as the same thing as the observer effect. However, they are not the same. Heisenberg Uncertainty is a mathematical limitation, whereas the observer effect is a physical limitation. Heisenberg uncertainty means that we cannot calculate complementary variables. Observer effect means that we cannot measure a complementary variable without disrupting the other complementary variable.

Chapter 7: The Structure of the Atom

The Born Interpretation: Probabilistic Mechanics

Since we cannot know the position and momentum of the electron simultaneously, we describe the electron in terms of probability. The wavefunction describes the behavior of the electron, and multiplying the wave function evaluated at a given point by the wave function's complex conjugate at that given point, multiplied by a small volume, yields the probability of finding the electron in the volume directly around that given point. The complex conjugate is denoted by a star.

$$\text{Probability around a point} = [\Psi(x, y, z)][\Psi^*(x, y, z)]\mathrm{d}x\mathrm{d}y\mathrm{d}z$$

Where dx, dy, and dz are very small x, y, and z. Thus, $\mathrm{d}x\mathrm{d}y\mathrm{d}z$ is a very small volume, $\mathrm{d}V$. Also, the reason why we multiply the wavefunction by its complex conjugate is because multiplying a real or imaginary number by its complex conjugate yields a positive number with physical significance. With $i = \sqrt{-1}$, the complex conjugate of a+bi is a-bi and vice versa. Thus, $(a + bi)(a - bi)$ is the same as

$$\left(a + b\sqrt{-1}\right)\left(a - b\sqrt{-1}\right) = a^2 + ab\sqrt{-1} - ab\sqrt{-1} - b^2\left(\sqrt{-1}\right)^2 = a^2 + b^2$$

If the wavefunction does not have an imaginary part, then multiplying by the complex conjugate is just multiplying by itself, because a+0i is the complex conjugate of a-0i, are both equal to a, thus resulting in a^2 when multiplied.

Orbitals and Orbital Boundary Surfaces

The volume in which the electron can be in is called an orbital. The regions where the electron cannot possibly exist in are called nodes, and they have an electron probability density value of zero. The wave function is zero at nodes. Usually, electrons can exist in a very large volume. For example, in most cases, the electron may exist from -∞ to ∞ in the x, y, and z direction. Thus, that electron can be anywhere in space, even galaxies away! Say, we pick the boundary to enclose where the electron is 90% of the time, or 95% of the time, or any arbitrary fraction of time. Or, we may choose a boundary where 90% or 95% of the electron exists. Both previous definitions of percentage existence of the electron are equivalent. Then, we draw a

Chapter 7: The Structure of the Atom

surface to represent the area that the electron is most likely in. By doing so, we just established something called an orbital boundary surface.

Orbital s ($\ell = 0$, $m_\ell = 0$)
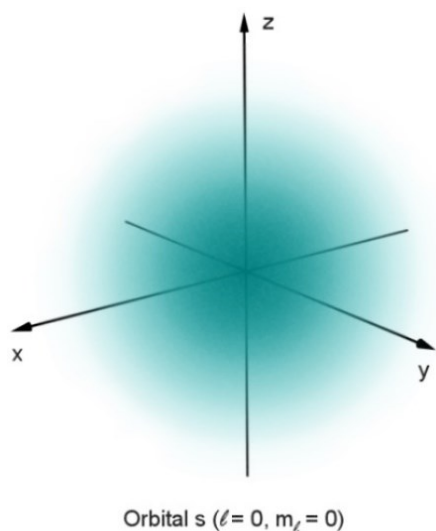
Figure 7.25. An s orbital density distribution. Darker shading means a higher probability that the electron is there. Note that although the probability of finding the electron decreases as we move away from the nucleus, the probability of finding the electron is nonzero, even when we are very far away from the nucleus.

Usually, when we use a wavefunction, we multiply it by a constant to ensure that the probability of the electron existing in all space is equal to one. This is called normalization, and it means is that the probability of finding that electron that exists in the universe is 1, confirming that it is always somewhere.

Electron Density

Although many times we represent bonds with lines, and assign two electrons to the bond, theoretical calculations indicate that the electron density between two atoms that are bonded is about 0.1 for a single bond, 0.2 for a double bond, and 0.3 for a triple bond, which is about $1/20^{th}$ of the number of electrons assigned to the bond. Now, you may ask, why aren't double bonds twice as strong as single bonds, nor triple bonds three times as strong as single bonds when we compare their bond energies? The reason that multiple bonds are always weaker than the corresponding multiple of single bonds, is because the electrons repel each other and weaken the bond because they have the same charge. An alternative way that is commonly used

Chapter 7: The Structure of the Atom

to explain this is to apply valence bond theory, with pi bonding, or to apply valence bond theory, with bent or tau (aka banana bonds), where overlap volume is reduced by geometric constraints.
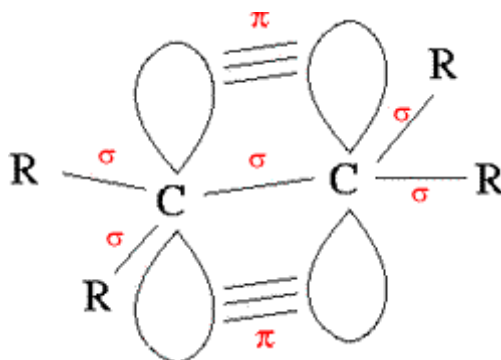
Figure 7.26. According to Erich Hückel's valence bond theory, single bonds are represented by a sigma (σ) bond, and double bonds are represented by a sigma and a pi (π) bond. This puts a geometric constraint on the double bond (double bonds generally require energy to rotate), and also explains why double bonds are not as strong as two single bonds (due to the smaller overlap of the p orbitals involved in the pi bond).

Separation of the Wavefunction to Simplify Calculations

In most cases, the wavefunction is easier to solve in polar spherical coordinates than in the linear Cartesian coordinates, because atoms are roughly spherical. We rewrite the wavefunction, $\Psi(x, y, z)$, in terms of r, a radius from the origin, θ, an angle from the positive z-axis, and ϕ, an angle from the positive x-axis which lies in the xy coordinate plane. Thus, we obtain $\Psi(r, \theta, \phi)$.

Chapter 7: The Structure of the Atom
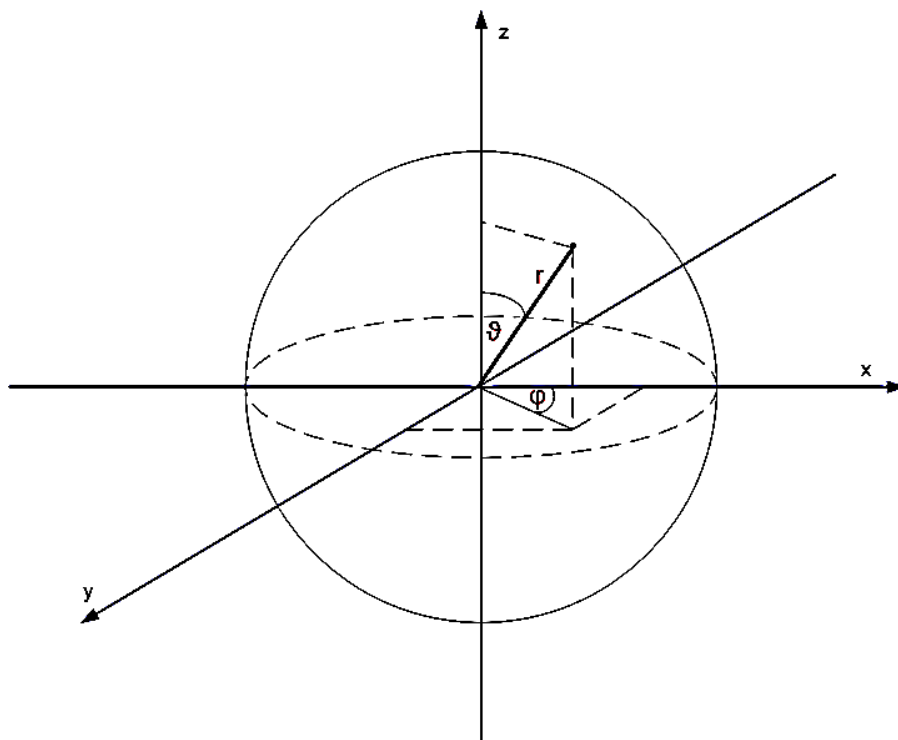
Figure 7.27. The Spherical Polar Coordinate System, where a point is located by its radius from the origin, r, its angle from the positive z axis, $\boldsymbol{\theta}$, and its angle from the positive x axis, $\boldsymbol{\phi}$.

We can separate the variables and factor out a radial and an angular wave function, which we can proceed to separate the two angular components. Thus, $\Psi(r, \theta, \phi) = R(r)A(\theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$. Then, we can graph the wavefunctions. Orbitals are the set of all positions where the electron might be, and they are represented by our surface boundaries. Although the electron has an equal probability of being in the separate lobes of its orbital, the lobes of an orbital can have either a positive or negative phase, which is important for bonding. Constructive interference is responsible for bonding interactions, which occur when orbitals align and overlap with the same phase, and destructive interference is responsible for antibonding interactions, which occur when orbitals align and overlap with opposite phases.

Chapter 7: The Structure of the Atom

Orbitals of the Atom

Quantum Numbers

Each electron in the atom can be completely described by four quantum numbers. Three are characteristics of the orbital the electron is in, and the fourth is a property of the electron itself.

The first three are the principle "energy level" quantum number, n, the azimuthal aka "angular momentum" aka "shape" quantum number, l, and the magnetic "space" quantum number, m_l. These three describe the energy level, shape, and the spatial orientation of the orbital that the electron resides in. Depending on the values of these three quantum numbers, the orbital is named differently. Usually, the orbital is designated by a number, followed by a letter, with a subscript which indicates its orientation in space. For example, the $3d_{x^2-y^2}$ orbital.

Radius from the Nucleus: The Principle Quantum Number, *n*

The first quantum number is the principle quantum number, n. For each increase in the principle quantum number, there is an additional type of orbital that is permitted. Principle quantum numbers are integers that begin at $n=1$ (ex: $n=1, 2, 3, 4$, etc.), and the number of types of orbitals is equal to the principle quantum number. Generally, the principle quantum number denotes the energy level of an electron, because it is related to the distance of the electron density from the nucleus.

Shape: The Azimuthal Quantum Number, *l*

There are four common types of orbitals, each designated by a letter, and each type of orbital has an azimuthal quantum number, l, that determines shape. The azimuthal quantum number begins at $l=0$, and for a given principle quantum number, the azimuthal quantum number may be any integer value from 0 to $n-1$. Thus, for $n=1$, only $l=0$ is possible. For $n=2$, $l=0$ and $l=1$ are possible. For $n=3$, l can be 0, 1, or 2. For all other values of n, the pattern continues. The four common orbitals are the sharp (s), principle (p), diffuse (d), and fundamental (f) orbitals, and they correspond to $l= 0, 1, 2$, and 3 respectively. The names for these orbitals originate from spectroscopy. For a principle quantum number n, the azimuthal quantum number, l, denotes

Chapter 7: The Structure of the Atom

orbitals of the same type and energy, and serves to separate the orbitals of a single principle quantum number by energy. Higher orbitals exist, but are insignificant, and are named g, h, i, j, k, and so forth. For single-electron systems, the Schrodinger equation can be solved exactly. For multi-electron systems, however, the Schrodinger equation cannot be solved exactly for the orbitals. With modern computing and molecular modeling, we can approximate the solutions to the wave function that yields the orbitals.
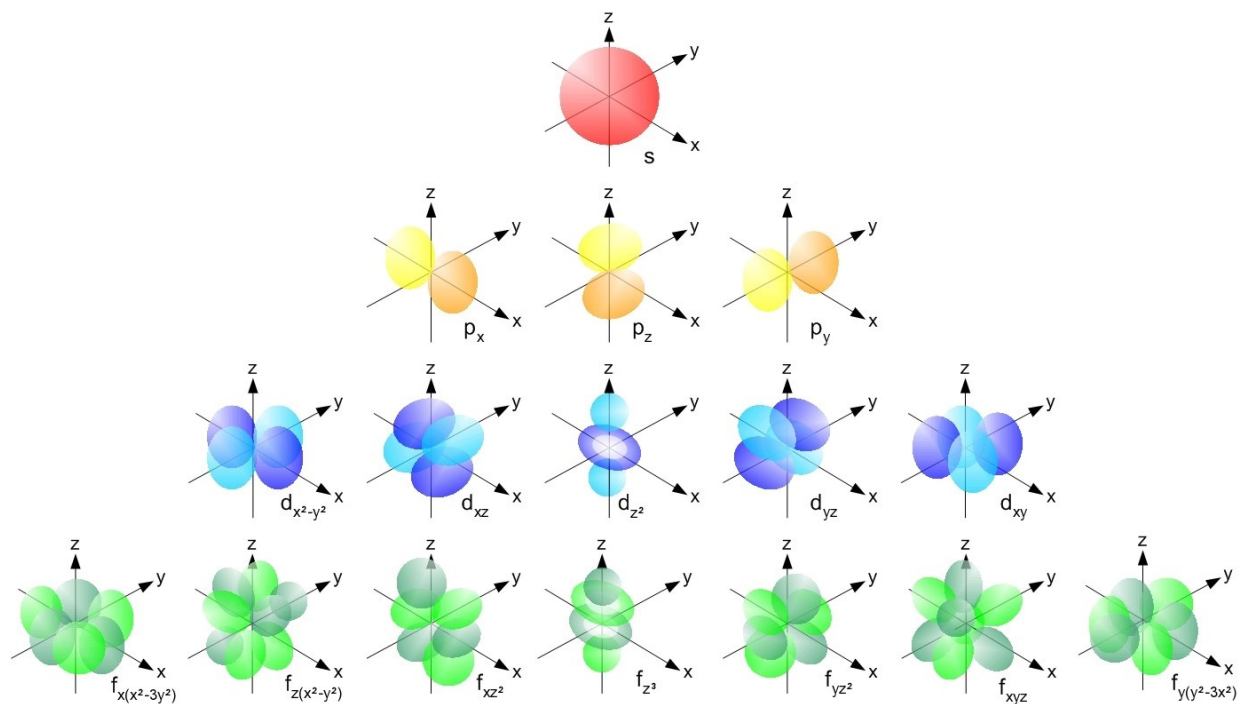
Figure 7.28. Different types of orbitals. For l=1, there is one s orbital. For l=2, there are 3 p orbitals, one along each axis. For l=3, there are five d orbitals. For l=4, there are seven g orbitals. Then, we just name the orbitals with higher values of l in alphabetic order.

Orientation in Space: The Magnetic Quantum Number, m_l

The letters after the type of orbital designate the orientation in space of the orbital, and depend upon the magnetic quantum number m_l. Since all orbitals with the same principle quantum number and azimuthal quantum number have the same energy, they are said to be degenerate. Thus, assigning a magnetic quantum number to each orbital does not make any difference in energy. The only rule is that each orbital of the same type and principle quantum number must have a different magnetic quantum number. For example, the $2p_z$ orbital is

Chapter 7: The Structure of the Atom

arbitrarily defined to have $m_l = 0$ for convenience. The magnetic quantum number for an orbital can have any integer value between $+l$ and $-l$. Thus, there is 1 s orbital (l=0), 3 p orbitals (l=1), 5 d orbitals (l=2), and so forth, and the s orbital has a $m_l = 0$, the p orbitals have $m_l = -1, 0, 1$, and the d orbitals have $m_l = -2, -1, 0, 1, 2$, and so forth. This also means that the number of total orbitals for a given principle quantum number n is equal to n^2.

Electrons Don't Spin. They Have Spin. The Electron Spin Quantum Number, m_s

Some Unknown Half-Integer Angular Momentum: The Stern-Gerlach Experiment

The fourth quantum number, the electron spin quantum number, m_s, describes an intrinsic property of the electron. Normally, when atoms are placed in a magnetic field, the spectral lines split in accordance to the equations that describe what is known as the Zeeman effect, thus producing an odd number of spectral lines. However, when certain atoms with odd periodic numbers were subjected to the magnetic field, something odd happened. An even number of spectral lines were generated! This anomalous Zeeman effect meant that there must be something with a half-integer angular momentum somewhere in the atom, and that something corresponded with atomic number. When Otto Stern and Walther Gerlach performed their experiment in 1921, and shot a stream of silver atoms through a magnetic field, the silver atoms split into two streams. They used silver because silver atoms have an unpaired electron in the 5s orbital. S orbitals, being spherically symmetric, usually do not have an angular momentum associated with them. Thus, the angular momentum must be from the unpaired electron, or something else unknown.

Chapter 7: The Structure of the Atom
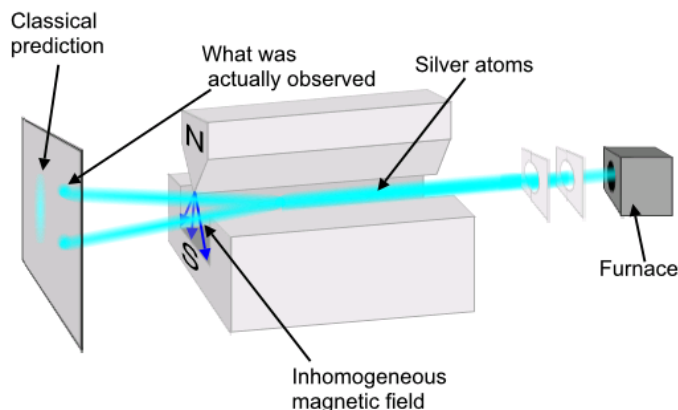
Figure 7.29. A diagram of the Stern Gerlach Experiment. The splitting of the silver atom beam demonstrated that the electrons had a property called spin, that causes them to interact with the magnetic field.

The Electron is a Fermion: The Pauli Exclusion Principle

Certain particles in physics, called fermions, have a half-integer spin that is either positive or negative. Fermions obey the Pauli exclusion principle, an idea Wolfgang Pauli first proposed for electrons in 1925, and later generalized to all fermions. In 1925, George Uhlenbeck and Samuel Goudsmit, in accordance with the Pauli exclusion principle, first proposed that the electron has a half-integer quality that Pauli later termed "spin". Note that this spin does not have a classical analogue, because the electron is not physically "spinning" in the classical sense. Thus, "spin" is a characteristic like mass and charge. The spin of the electron is indeed half integer, as proven by Paul Dirac in 1928 with his relativistic quantum mechanics, and electron spins come in the positive and negative variety, $m_s = -\frac{1}{2}$ or $m_s = +\frac{1}{2}$. Being a fermion, the electron follows the Pauli exclusion principle, which says that no two fermions can have the same set of quantum numbers. Therefore, each orbital, described by an *n*, *l*, and a m_l, can only contain a maximum of two electrons, which must have opposite spins, one with a spin of $+\frac{1}{2}$, and another with a spin of $-\frac{1}{2}$. Although there is normally no difference in the energy or behavior of electrons with different spins in the same orbital, in the presence of an electric field or an electric current and a magnetic field, the two electrons indeed have different energies, as shown by the Zeeman effect, the anomalous Zeeman effect (odd atomic number), and other similar phenomena.

Chapter 7: The Structure of the Atom
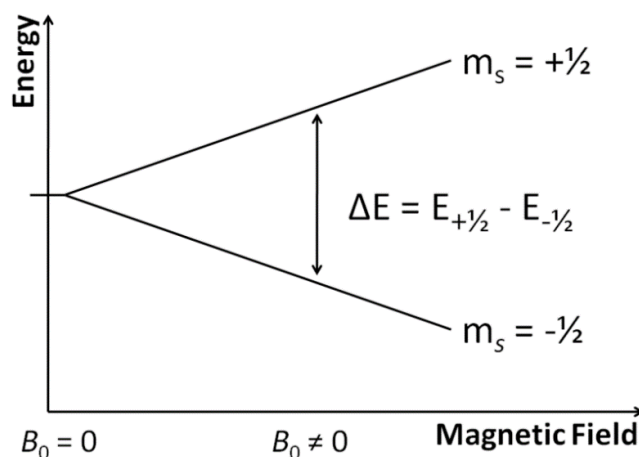
Figure 7.30. Two electrons in the same atom and the same orbital usually have the same energy and are said to be degenerate. However, when the atom is placed in the presence of a magnetic field, the energies of the two electrons become different.

Shapes and Nodes of the Orbitals

The Spherical Sharp Orbitals

The s orbitals of a given principle quantum number is always the lowest in energy. There is one s orbital for each principle quantum number. S orbitals are spherically symmetrical, and have no nodal planes (angular nodes), which we will encounter in the p and the d orbitals. Rather, the s orbitals only have spherical (radial) nodes, at set radii from the nucleus. The 1s orbital has no nodes, the 2s orbital has one node, the 3s orbital has 2 nodes, and so forth. The ns orbitals have n-1 spherical nodes, where their electron density falls to zero.
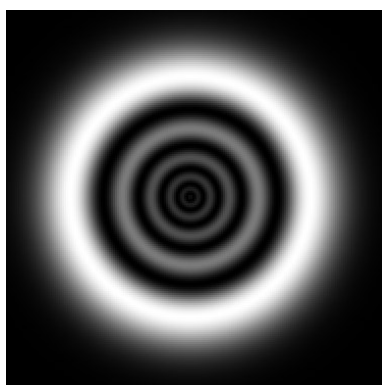
Figure 7.31. A S-orbital picture. Note the spherical symmetry. There is 1 s orbital for each principle quantum number, n.

Chapter 7: The Structure of the Atom

The Perpendicular Principle Orbitals

There are three p orbitals for each *n*>1. The p orbitals lie along the x, y, and z axis, and are symmetric about the axis they lie on. They also are symmetric about the nucleus, and have two lobes that have the same geometry. The p orbitals are orthogonal (perpendicular) to a "nodal plane" that passes through the nucleus and separates the two lobes. This nodal plane is an angular node, as the electron density is zero in the space which is 90 degrees from the axis that the p orbital is on. The p orbitals also have a radial node, which is analogous to the spherical nodes of the s orbitals. At a certain radius from the nucleus, the electron density falls to zero in a radial node. The p orbitals all have a single planar node, and one radial node for each *n*>2. Thus, a 2p orbital has a planar node, a 3p orbital has a planar node and a radial node, a 4p orbital has a planar node and two radial nodes, and so forth. Thus, p orbitals also have *n*-1 nodes. Note that there are no 1p orbitals, because an azimuthal quantum number of 1 is not permitted for *n*=1.
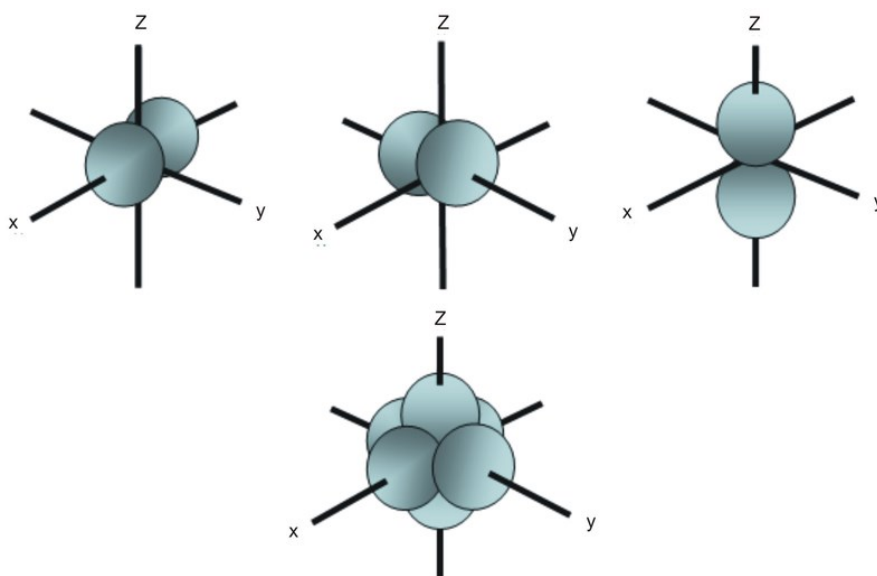
Figure 7.32. A diagram of the three p orbitals. Note that each lies along an axis, and are all 90 degrees to each other. Thus, the diagram under the three individual orbitals illustrates all three orbitals together.

The Diffuse Orbitals

There are five d orbitals for each *n*>2. Three d orbitals lie in the xy (d_{xy}), yz (d_{yz}), and xz planes (d_{yz}), one lies on the x and y axes ($d_{x^2-y^2}$), and the last one is around the z axis (d_{z^2}). The d orbitals have 4 lobes each, and although they may vary in appearance, the d orbitals of a principle quantum number are degenerate, and have the same energy. The 3d orbitals have 2

Chapter 7: The Structure of the Atom

angular nodes each. The xy, yz, xz, and the $x^2 - y^2$ orbitals have 2 nodal planes each, and the z^2 has a nodal plane orthogonal to the z axis, along with a cone-shaped node which radiates from the nucleus and surrounds the z axis. The cone-shaped node is an angular node, as the cone represents all points that are a certain angle from the z axis. As we increase the principle quantum number, for each principle quantum number above 3 there is another radial node added. Thus, d orbitals also have n-1 nodes.
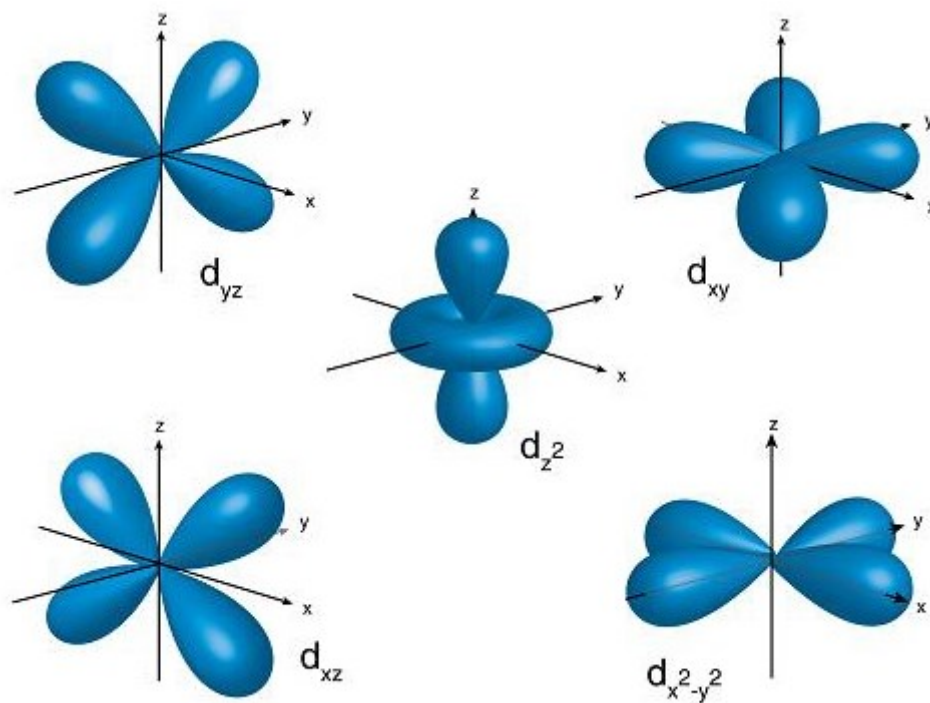
Figure 7.33. The five d orbitals. Note that yz, xy, and xz are on the corresponding planes but not on the axes, x^2-y^2 is on xy axes, and z^2 is shaped like a donut with two lobes protruding out of the center.

All the Rest

There are seven f orbitals, and they are relatively insignificant in the bonding experienced in general and organic chemistry. Let's leave them to the advanced inorganic dude. Likewise, there are 9 g orbitals. Later orbitals are just named in alphabetic order.

Chapter 7: The Structure of the Atom

Relative Energies of the Orbitals

Electrostatic Interactions and Energy

The orbitals have distinct properties, based upon their radius from the nucleus, and their geometry. Orbitals closer to the nucleus and with less nodes tend to have lower energies than orbitals farther away from the nucleus and with more nodes. Although many laws do not apply at the quantum scale, Coulomb's law of electrostatic interaction still holds, even though the particles are tiny.

We define the energy of an electron to be zero when the distance between the proton and the electron is infinity. However, when they get closer and closer, the electron and the proton liberate energy, because they have opposite charges and bond together. Thus, the energy of the electron and proton after we bring them together is negative. Repulsions among the electrons raise the energy of the atom, and higher energies tends to be less stable. Stable bonding in Chemistry always liberates energy, and breaking stable bonds require energy.

The Aufbau Principle

The orbitals are arranged in the order of energy, and the electrons generally fill the energy levels in the same order, as shown on the periodic table. This is known as the Aufbau principle, where orbitals are occupied sequentially from lower to higher energy to provide a stable electronic configuration. The Aufbauprinzip, or the building-up principle, was originally created by Niels Bohr and Wolfgang Pauli in the early 1920's, and in short, it means that orbitals are filled up by the order of energy, from lowest to highest, and the orbitals are occupied as follows:

$1s < 2s < 2p < 3s < 3p < 4s \approx 3d < 4p < 5s \approx 4d < 5p < 6s \cong 4f \approx 5d < 6p < 7s \cong 5f \approx 6d < 7p$ and so on

Chapter 7: The Structure of the Atom
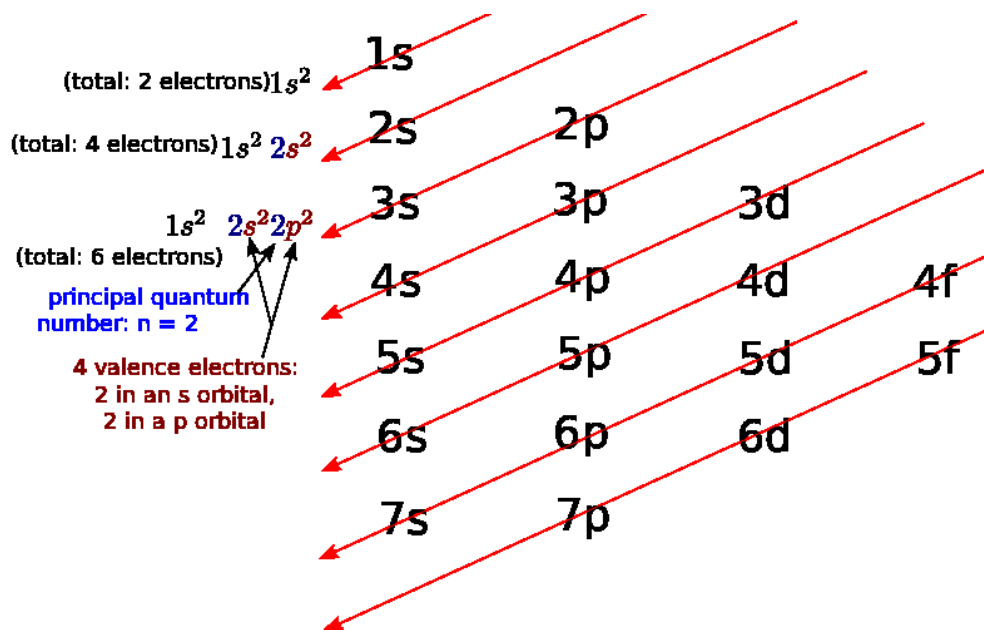
Figure 7.34. Orbital filling according to the Aufbau Principle, and also with electron configuration written out.

In 1927, Charles Janet stated that the orbitals are filled in order based upon the value of $n+l$. The orbitals do indeed fill from those with lower $n+l$ values to those with higher $n+l$ values. In 1936, Erwin Madelung formally proposed his set of rules based upon spectroscopic data, and the Aufbau principle is most commonly known as the Madelung energy ordering rule. The rule is empirical, and only applies to neutral atoms.
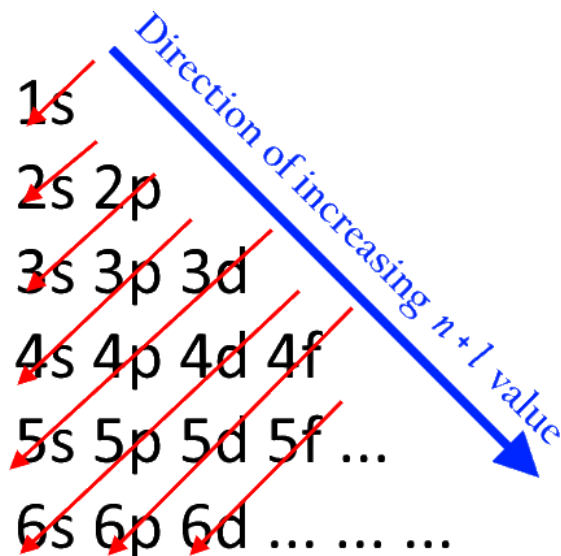
Figure 7.35. The orbital filling order, which corresponds to the diagonals drawn in the order of increasing n+l value.

Chapter 7: The Structure of the Atom

Penetration Effects

The reason that the energies of the ns electrons are lower than the $(n-1)$d electrons of a lower principle quantum number before electrons occupy the $(n-1)$d orbitals is because electrons in s orbitals can "penetrate" and approach the nucleus more frequently than the $(n-1)$d orbitals, even though they are being shielded by electrons in lower energy orbitals. There is a s orbital density peak further inside than the peak of the $(n-1)$d orbital density. The same applies for the relation between the ns electrons and the $(n-2)$f electrons. However, note that once the $(n-1)$d electrons and the $(n-2)$f electrons are added, the energy of the ns electron then becomes higher than the $(n-1)$d and the $(n-2)$f electrons, because the ns electrons now are farther away from the nucleus.

The p orbitals, which are not spherically symmetric, do not have such a large density close to the nucleus, and thus are higher in energy. The p orbitals have decreasing electron density as the angle increases from the axis that they are on, and the p orbitals have zero electron density at the nucleus and at any position in space on the plane that is orthogonal (perpendicular) to the axis that they are on. Thus, np orbitals do not have significant penetrating interactions that can lower their energy below that of the $(n-1)$d orbitals when the $(n-1)$d orbitals are unoccupied, but do have enough to lower their energy below the $(n-1)$f orbitals when the $(n-1)$f orbitals are unoccupied.

Hund's Rules
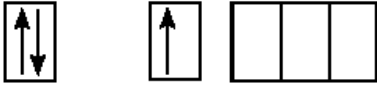
Since each orbital can contain 2 electrons in accordance with the Pauli exclusion principle, there are 3 configurations electrons can occupy an orbital. Up and down are terms used to describe particles with spins of $+\frac{1}{2}$ and $-\frac{1}{2}$. Therefore, there can either be a single up electron, a single down electron, or an up and a down electron which are said to be spin paired. There cannot be 2 electrons of the same spin in the same orbital, because that violates the Pauli exclusion principle, as two electrons in the same orbital with the same spin have the same four quantum numbers. Although the orbitals of the same quantum number and type are degenerate when they are all empty, all half occupied, or all fully occupied, they have energy differences

Chapter 7: The Structure of the Atom

when the orbitals do not have the same number of electrons, due to repulsions between the electrons. Thus, to minimize repulsions when filling up a set of degenerate orbitals, the electrons follow Hund's rules. Friedrich Hund formulated his set of rules in 1927, two years after the confirmation that electrons had spin. Hund's rules are normally simplified into the following statement:

Electrons first half-fill degenerate orbitals, and then they fully fill the orbitals. This is because electrons in the same orbital encounter more unfavorable repulsion.
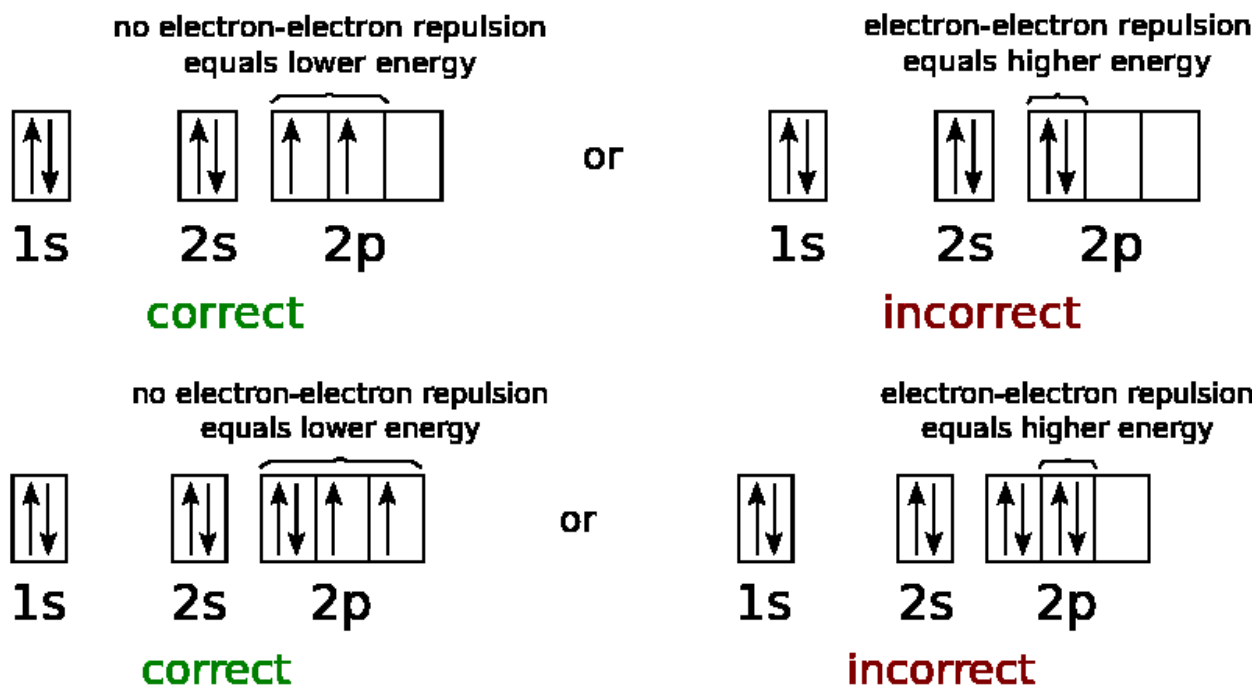
When half-filling the degenerate orbitals, the electrons are all the same spin, and later, when the orbitals are being filled, the electrons "spin pair" to yield two electrons, one up and one down, in each orbital.

Chapter 7: The Structure of the Atom

a. [↑↓] [↑] [ ][ ][ ]   correct
   1s   2s   2p

b. [↑↓] [↑↓] [↓][ ][ ]   correct
   1s   2s   2p   (since this is the 1 electron in the p sublevel
                          it can be either "spin-up" or "spin-down")

c. [↑↓] [↑↓] [↑][↓][ ]   incorrect
   1s   2s   2p   (the spin of the 2nd electron depends on the spin of the
                          1st electron, even though they aren't in the same orbital)

d. [↑↓] [↑↓] [↑][↑][ ]   correct
   1s   2s   2p   (as long as you draw the first electron in each orbital as
                          "spin-up", you will draw a correct orbital diagram)

If the electron does not follow Hund's rules, then an additional amount of energy must be provided, which is the exchange energy. The excess exchange energy must be supplied, which in turn destabilizes the atom. Thus, in unexcited atoms, Hund's rules are followed.

Electronic Configuration

The Ground State Electronic Configuration

Hund's rules, the Aufbau principle, and the Pauli exclusion principle together explain how electrons are placed in an atom. This natural configuration of the single atom of an unexcited element is called the ground state electronic configuration.

We write the electronic configuration of the atoms as follows:

1. We write the orbitals occupied, followed by a superscript which indicates how many electrons are in the orbitals.
   a. Ex: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$ for vanadium
2. We can write the electron configuration with a short-hand notation by starting at a noble gas, and continuing from there.
   a. Ex: $[Ar]4s^2 3d^3$ for vanadium

Chapter 7: The Structure of the Atom

Exceptions to the Aufbau Principle

Although in general the electrons of atoms in ground state electron configuration follow the Pauli exclusion principle, Hund's rules, and the Aufbau principle, there are a few exceptions to the Aufbau principle, because the Aufbau principle only a rule of thumb. There are no exceptions to the Pauli exclusion principle, because it is a physical law, and unexcited atoms do not violate Hund's rules because of unfavorable exchange energy. The following discussion only applies to deviations from predictions made by the Aufbau principle.

The electron configurations in the lower d block and the f block are not quite in good accordance to the Aufbau principle, because the f and d orbitals are approximately the same energy, so there is not much difference on which orbital is occupied first. Also, some notable exceptions in the upper d-block occur in groups 6 (VIB) and 11 (IB). In group 6, the half-filled d orbitals provide an extra amount of stability, as the interchangeable electrons with the same spin are perfectly symmetrical and resonate constructively with each other, thus, releasing a very small amount of energy that makes the $(n+1)\text{s}^1 n\text{d}^5$ configuration more favorable than the $(n+1)\text{s}^2 n\text{d}^4$ configuration. Likewise, the same applies to group 11, except the effect is even stronger due to spin pairing. Thus, Cr and Mo in group 6 have a $(n+1)\text{s}^1 n\text{d}^5$ instead of a $(n+1)\text{s}^2 n\text{d}^4$ configuration, and Cu, Ag, and Au have a $(n+1)\text{s}^1 n\text{d}^{10}$ configuration instead of a $(n+1)\text{s}^2 n\text{d}^9$ configuration.

Ionization

When atoms are ionized, they do not completely follow the Aufbau principle, because the Aufbau principle is only relevant for electrons of neutral atoms in ground state electron configuration. In cation formation, the np electrons are removed before the ns electrons if they have the same quantum number. For atoms in the d-block, the ns electrons with a higher principle quantum number are removed first. For example, if we are ionizing a titanium atom to an Ti(IV) ion, to get from Ti to Ti^{4+}, we first remove the two 4s electrons before removing the two d electrons. Thus, we go from $[\text{Ar}]4\text{s}^2 3\text{d}^2 \rightarrow [\text{Ar}]4\text{s}^1 3\text{d}^2 \rightarrow [\text{Ar}]4\text{s}^0 3\text{d}^2 \rightarrow [\text{Ar}]3\text{d}^1 \rightarrow [\text{Ar}]3\text{d}^0 = [\text{Ar}]$. and arrive at the final electronic configuration, which is the same as

Chapter 7: The Structure of the Atom

that of an argon atom. Similarly, we are ionizing an atom from the p block where $n \geq 4$, we first remove the np electrons, then the ns electrons, then the $(n\text{-}1)$d electrons.

The reason for this is because of the orbital radius, which according to Coulomb's law correspond to how strongly the electrons are bound. Although the $(n\text{-}1)$d electrons are slightly higher in energy than the ns electrons during the filling of the orbitals, the ns electrons, which are farther from the nucleus, have lower attraction to the nucleus. Thus, for an atom in ground state electron configuration, the ns electrons become higher in energy than the $(n\text{-}1)$d electrons after the $(n\text{-}1)$d orbitals become occupied. Therefore, the ns electrons are bound less tightly, and are easier to remove from the atom. Also, although the When electrons are provided, the cation will be reduced back to the element in the opposite order that the electrons were lost. In anion formation, the order that electrons are added tends to follow the Aufbau principle, and thus, is not very problematic. Also, it is difficult to have many electrons added to most atoms due to repulsion, so monoatomic anions with high charges are quite rare in nature.

Magnetism

One type of phenomena that the electronic configuration rules explain is magnetism. Paramagnetism is an effect observed for elements and compounds with an unpaired electron. Paramagnetic materials are attracted to magnetic fields. For example, lithium is paramagnetic because of the unpaired 2s electron. Iron has 4 unpaired d orbital electrons, making iron ferromagnetic, which is observed when the paramagnetic electrons are all locked into the same alignment. Paramagnetism is when the material is magnetized in the presence of a magnetic field. Ferromagnetism is when the material is magnetized in the presence of a magnetic field, and retains the magnetic properties after the magnetic field is removed. To be ferromagnetic, a material must also be paramagnetic.

Chapter 7: The Structure of the Atom
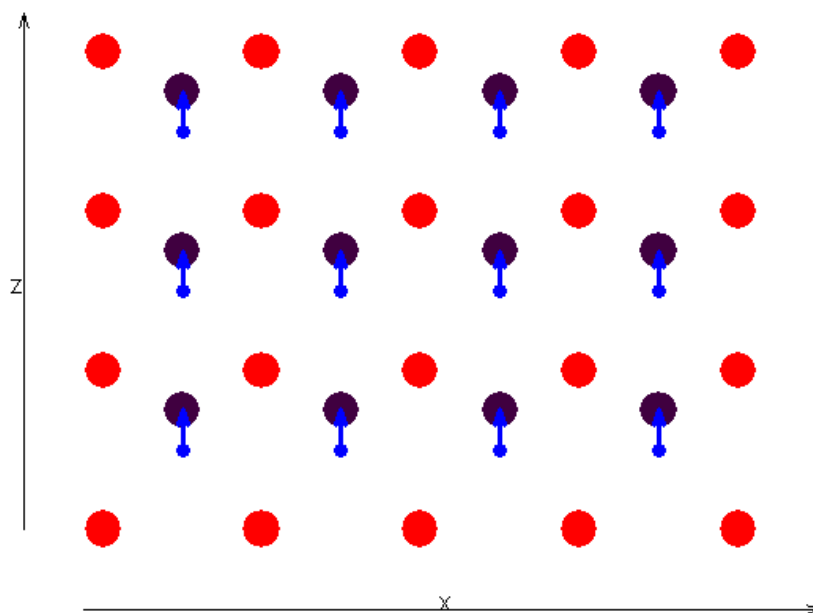
Figure 7.36. For ferromagnetic materials, the spins are all aligned even in the absence of a magnetic field.

Earth has a natural magnetic field, generated when the iron-rich earth revolves around. When paramagnetic substances revolve around, they generate a magnetic field. When the iron cools underneath the earth, it aligns itself to earth's magnetic field and becomes magnetic, thus forming magnetite. The opposite effect is diamagnetism, and this is observed for atoms with no unpaired electrons. When the electrons are all spin-paired, they form a stable configuration, which resists the influence of the magnetic field. Thus, diamagnetic materials are repelled from magnetic fields. An example would be beryllium, which has all of its electrons paired.

However, not all elements with a ground state electronic configuration with an unpaired electron are paramagnetic, and not all elements with a ground state electronic configuration without unpaired electrons are diamagnetic, because when they bond with other atoms, sometimes themselves, the electron configurations change, and they lose their magnetic properties. In the case of bonding, the magnetic properties would depend on the electron configurations of the molecules of the material. Also, some materials change properties based upon the magnetic field applied, because the magnetic field can shift electronic configurations by changing the energies of the orbitals.

Chapter 7: The Structure of the Atom

Discovery of the Neutron

An Unknown Source of Mass

In 1932, after the electron and proton were discovered, the third main subatomic particle, the neutron, was formally discovered by James Chadwick. The neutron is necessary for atomic theory at the time, because it accounts for the additional mass of the atom that is not from the protons and electrons. Rutherford had already confirmed his hypothesis that there were massive particles at the center of the nucleus by "splitting the atom" in 1917. What did not add up was that there was often an excess of mass that cannot be explained by a combination of only electrons and protons, and that the excess of mass was inconsistent in different isotopes of one element. Knowing that his early hypothesis that the nucleus was composed of helium nuclei was certainly wrong, Rutherford proposed in 1920 that there may be a neutral particle in the nucleus that may be composed of a proton-electron pair. However, the mass of a proton-electron pair does not correspond very well to the mass of the hypothetical neutron, and thus causes a discrepancy, leading to his later proposal that there was a different particle in the nucleus altogether, that has a mass similar to that of the proton.

The Bothe Becker Experiment

Previously, in 1930, Walther Bothe and Herbert Becker used alpha particles from polonium to bombard beryllium, boron, and lithium targets. They found a new type of radiation that was not previously observed. They thought that the non-ionizing highly penetrating radiation was a form of gamma ray, because the radiation was not deflected by a magnetic field. However, gamma rays cannot penetrate a few millimeters of lead, but the new form of radiation could penetrate a fifth of a meter! Thus, they attributed the emission to ultra-high energy gamma rays.

The Curie-Curie Experiment

In 1932, Irène and Frédéric Joliot-Curie used radiation from polonium that was reemitted from a beryllium target to knock out protons from paraffin. The Joliot-Curies believed that gamma rays knocked out the protons. However, when they measured the speed of the emitted

Chapter 7: The Structure of the Atom

protons by measuring their range in air, they found the range of the protons to be about 0.26 metres, which corresponded to an ejection velocity of $3 * 10^7 \frac{m}{s}$. For the protons to be traveling that fast, they needed to have an extremely high energy of about 50 MeV. This also meant that the radiation that displaced the protons needed to supply a minimum of that energy.
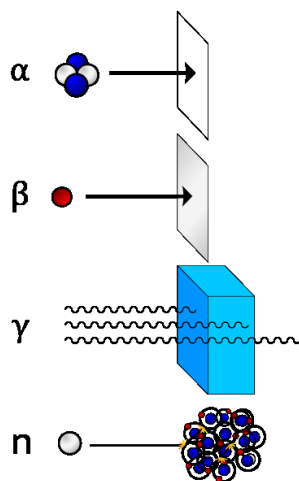
Figure 7.37. Alpha particles can be stopped by a sheet of paper. Beta particles can be stopped by a thin sheet of lead. Gamma rays can be stopped by a few inches of lead. High speed and energy neutrons can penetrate up to a fifth of a meter of lead. Because neutrons have no charge and experience no repulsion from positively charged protons, they can strike and fragment the nuclei of atoms by dislodging protons and nuclei of lighter elements.

Chadwick's Experiment

When Chadwick came across their results and told Rutherford, they repeated the experiment, and resulted in a similar value of 52 MeV. One electron-Volt (eV) is the amount of energy that an electron gains when it falls through a potential difference of one volt. 1 eV is equal to $1.6021 * 10^{-19}$ J. Although it does not seem very much, a mega-electron-Volt (MeV) is an energy unit that is approximately $1.602 * 10^{-13}$ J, which is a very large amount of energy for a subatomic particle, especially if you have many of those particles. Chadwick then calculated that the energy cannot be supplied by photons, because the quantum theory of light does not permit photons with an energy of above 14 MeV, thus leading to speculation that the effects could be explained by attributing the radiation to the hypothetical neutron. Rutherford and Chadwick believed that neutrons were responsible for displacing the protons because neutrons, with a similar mass to protons, needed far less velocity to be able to remove the protons from the paraffin.

Chapter 7: The Structure of the Atom

Chadwick set to work immediately, because the discovery would be time-sensitive. He used a cylinder to produce his hypothetical neutrons by exciting beryllium with radiation emitted by polonium. Polonium is an alpha emitter. Beryllium normally does not undergo nuclear reactions, but when excited by the alpha particles, it releases the strange new form of radiation. Chadwick observed that this form of radiation not only led to proton ejection, but also led to ejection of nuclei that corresponded to the lighter elements. Gamma rays could not possibly eject those heavier particles, because that would require even more energy. By measuring the change in momentum of Hydrogen and Nitrogen particles that were bombarded by these particles, Chadwick calculated the mass of the new particle that is responsible for the radiation to be approximately 1.15 ± 0.1 proton masses, and concluded that the particle was indeed the neutron they had been searching for. In retrospect, it makes good sense that the neutron can remove nucleons from a nucleus by means of impact. It was both massive and energetic enough to knock out the protons and other neutrons, and it bears no charge. Positively charged particles, such as protons, are deflected by the nucleus. The only common negatively charged particle, the electron, is not massive enough to make nuclear disintegration likely. However, the neutral neutron can penetrate the nucleus with ease, and is massive enough to cause the changes that were observed. Neutral particles are very difficult to detect, but Chadwick finally found the elusive neutron that Rutherford had sought after.

Chapter 7: The Structure of the Atom

Chapter 8: Kinetics and Equilibrium

As seen in the section describing gases, most common substances encountered can be seen as a collection of numerous particles, that have stochastic average properties. The sheer number of molecules ensures that, although variables such as velocity may change for a specific particle, the average of the variables assigned to the system is sufficiently constant to be measured. Thus, for most common samples of gases, the pressure may be measured, because the number of molecules is so large that it is difficult to imagine. To put this in perspective, the number of atoms in a liter of air is about 10^{24} , which is 10^6 or a million times the number of grains of sand on the face of the earth (10^{18}). All the actions of the individual particles are then averaged, to give the empirical properties of the gas. Thus, many calculations in chemistry are dependent upon the stochastic nature of the large number of particles.

Kinetics and Equilibrium

Previously, when we discussed systems, we talked about their properties when they are in a stable state. However, whenever a reaction occurs, many of the variables do not remain constant. Thus, if we need to know how long it takes for a reaction to take place or how fast the reaction will proceed, we need to use new techniques that deal with change. The field is appropriately called kinetics, because the Greek root "kinein" means having to do with motion. Then, when the reaction does not proceed any further, and the system becomes stable again, we can again apply thermodynamics and the concept of equilibrium.

Thermodynamic and Kinetic Favorability

Thermodynamic Favorability

As a result of the first and second laws of thermodynamics, chemical reactions only occur if the reaction is thermodynamically favorable. We have already seen two types of free energies, which allow for us to determine if a reaction will proceed. We will deal primarily with reactions at constant temperature and pressure, because reactions in open air are under constant pressure and most reactions occur in an open container. Thus, the Gibbs free energy is the focus of our

discussion. However, for reactions at constant temperature and volume, the Helmholtz free energy can be applied likewise. For a reaction to occur under normal circumstances, the change in Gibbs free energy must be negative, which indicates an increase in entropy for the universe. Note how we are concerned with change, and in this case, reactions only proceed if the reactants have more Gibbs free energy than the products.

$$\Delta G = G_{final} - G_{initial} = G_{products} - G_{reactants}$$

$$\Delta G \text{ is negative when } G_{products} < G_{reactants}$$

If the reaction that is proposed has a negative change in Gibbs free energy, the reaction is said to be thermodynamically favorable, and the reactants are said to be thermodynamically unstable with respect to the more thermodynamically stable products. This makes sense, because the system has a tendency to minimize its free energy, in order to reach a state of increased stability, which corresponds to a state of increased entropy for the universe. When the system achieves stability, also known as equilibrium, the system can no longer react. Note, however, that the thermodynamic stability may change if there is a change in temperature or other variables that affect energy which in turn affects temperature.

Kinetic Favorability

However, whether or not we observe the reaction is also dependent upon the kinetic favorability of the reaction. Kinetics has to deal with how fast the reaction occurs. We have already discussed that for a reaction to occur, the molecules involved in the reaction need to collide with sufficient energy and in the correct orientation, both of which are dependent on kinetic factors. As expected, reactions that are extremely slow are generally not observed to occur. Something very important to remember is that all substances that are thermodynamically stable are kinetically stable because no change occurs, but not all substances that are kinetically stable are thermodynamically stable. Because both thermodynamics and kinetics determine whether or not a reaction will occur, we can separate hypothetical reactions into four categories, depending upon thermodynamic favorability of the products relative to the reactants, and depending upon kinetic favorability of the reaction itself.

Chapter 8: Kinetics and Equilibrium

Types of Reactions, Based Upon Thermodynamic and Kinetic Favorability

Thermodynamically Unfavorable Reactions Are Simply Impossible

The first two types of hypothetical reactions are the simplest. When the reaction is thermodynamically unfavorable because the reactants are more stable than their products, the reaction simply does not occur, regardless of kinetic favorability. Since kinetics deal with change, and thermodynamically unfavorable reactions do not occur, kinetics is irrelevant because the reaction does not occur. Thus, thermodynamically unfavorable reactions that are kinetically favorable or unfavorable are purely hypothetical. The reactants are said to be nonlabile, or unlikely to change.

Thermodynamically Favorable but Kinetically Unfavorable Reactions Tend Not to Occur

The third type are reactions that are thermodynamically favorable, but kinetically unfavorable. For this type of reaction, the substances initially used in the reaction are nonlabile. In other words, although the reaction is allowed by the laws of thermodynamics, the molecules do not have a sufficient amount of thermal energy under normal conditions to begin the reaction. Thus, the molecules do not collide hard enough with each other and in the correct orientation to overcome the "activation energy" that needs to be provided for the reaction to proceed. However, if enough energy is added to overcome the activation energy, or if there is a catalyst that allows for the reaction to proceed by avoiding the pathway associated with the large activation energy that inhibits the reaction, the reaction may then proceed.

A Thermodynamically Unfavorable but Kinetically Stable Isotope is Called an Allotrope:

When the reaction is a change in allotrope that is thermodynamically favorable but kinetically unfavorable, the kinetically stable but thermodynamically unstable allotrope is said to be metastable with respect to conversion to the thermodynamically stable allotrope. A common example is the diamond, which is said to be forever. Although diamond is thermodynamically unstable with respect to conversion into graphite at STP, as demonstrated by the negative Gibbs free energy for the change in allotrope, diamonds are still common because the rate at which the

Chapter 8: Kinetics and Equilibrium

conversion occurs is so slow that diamonds are considered to be stable in most circumstances due the incredible stability of the carbon-carbon (C-C) covalent bonds. Covalent bonds usually require about $10^5 \frac{J}{mol}$ to break, which is very difficult to obtain from the kinetic energy of the molecules alone. Thus, diamond is said to be metastable under standard conditions. However, when additional energy or other chemicals are added, the activation energy can be overcome by supplying a sufficient amount of energy, as shown by Lavoisier in 1772 when he burned a diamond by focusing the rays of the sun using a huge magnifying glass and collected the carbon dioxide that resulted in order to prove that diamond was a form of carbon. Likewise, the reason why most reactions that can perpetuate themselves are strongly exothermic, is because of the fact that they can supply additional energy that can initiate more reactions. A good example of this is combustion, where fire "spreads" by heating the combustible materials next to the fire to a temperature that can destabilize the substance sufficiently to also "catch on fire."

Thermodynamically Favorable but Kinetically Unfavorable Reactions Occur in the Presence of a Catalyst, Which Allows for the Reaction to Proceed Through an Alternative Kinetically Favorable Pathway:

Many examples of thermodynamically favorable but kinetically unfavorable reactions are occurring in your cells right now. Most biological processes occur extremely slowly, but with the help of catalytic enzymes, the reactions occur millions or billions of times faster than if the reactants were simply mixed in a test tube. Because the reactions occur, we know that the reactions are thermodynamically favorable. However, if the reactions did not occur sufficiently fast, we would all not exist.

Thermodynamically and Kinetically Favorable Reactions Occur Easily and Frequently

The fourth type of reaction is both thermodynamically favorable and kinetically favorable. Because the reactants are unstable, we say that they are labile, or subject to change. That said, the reactions usually react rapidly at room temperature. Labile substances can have spectacular reactions, as demonstrated by the reaction of sodium and chlorine to form table salt. These reactions usually have very negative Gibbs free energies and low activation energies. With

Chapter 8: Kinetics and Equilibrium

a high thermodynamic "drive" to react, and with very little barrier to hinder reaction, these reactions occur quickly, and are typically those that we are interested in.

Concentration

By now, all of you should be familiar with the idea of concentration. Concentration is a measurement of how much of something there is in a given volume. The most commonly used unit of concentration is molarity, which is measured in moles per liter. In chemistry, we mainly use molarity, because it is convenient. Do note, however, that the volume changes based upon the temperature, because most things expand when heated, and shrink when cooled. Although the number of moles of substance does not change, the volume in liters does change, and it is expected that molarity is greater when the solution is cooler, because the decrease in volume leads to an increase in concentration as measured by molarity.

$$\text{Molarity} = \text{M} = \frac{\text{mol}_{\text{substance}}}{\text{L}_{\text{solution}}}$$

Molarity can also be used on gases, where the moles of substance is the moles of gas, and the volume is just the volume of space that the gas molecules are in. However, molarity for gases is very inaccurate, unless the pressure and the temperature are fixed. In the case of an ideal gas, we use the ideal gas equation we had before, $pV=nRT$. Density, ρ, for an ideal gas is a function of molar mass, M, pressure, p, and temperature, T. Thus, we have:

$$density = \frac{p\text{M}}{RT} = \rho, where \text{ M } is\ molar\ mass$$

Other measurements of concentration are also used, such as molality (moles per kilogram of solvent), or parts per million. We will not frequently encounter them, because the convention is to use molarity, but I agree with the fact that molality is superior to molarity in many aspects.

Rate of Reaction is Proportional to Number of Collisions

The field of chemical kinetics is centered around the study of the rate of chemical reactions, and is closely tied with chemical equilibrium, which we will cover simultaneously.

Chapter 8: Kinetics and Equilibrium

The field of kinetics is founded upon the observation that chemical reactions generally proceed faster when a greater concentration of a reagent (a reactant) is utilized. For example, magnesium becomes oxidized far more quickly in 12 molar HCl than in 2 molar HCl. If we imagine the molecules that are reacting, we see them zooming past one another, and occasionally colliding to react. Thus, it makes sense that if we increase the concentration of a reagent, there are more molecules of that chemical species in the same volume of solution. With more molecules zipping by, the likelihood of collision increases roughly proportionally with the concentration of the reagent.

Low concentration = Few collisions   High concentration = More collisions
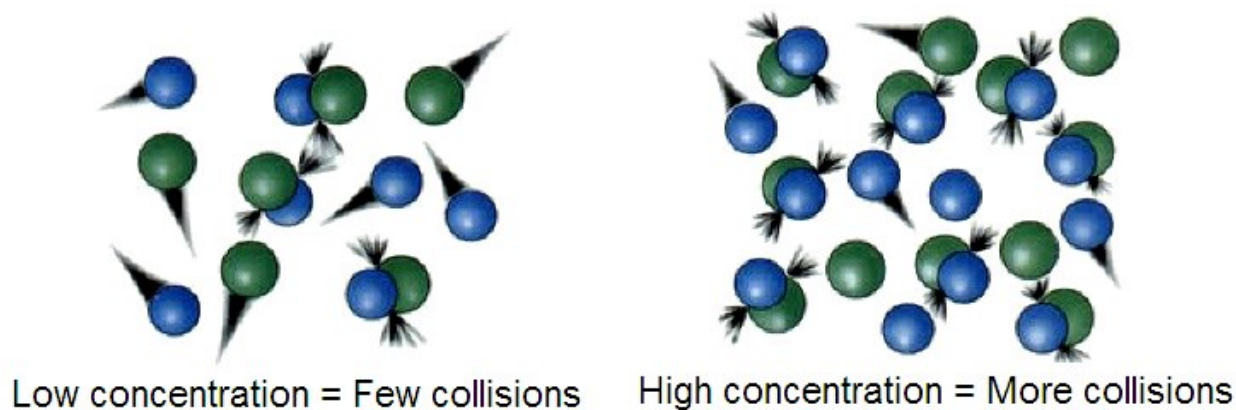
Figure 8.1. The higher the concentration, the more frequently collisions occur, the faster the reaction proceeds.

Example Reaction:

For example, take the following hypothetical one-step reaction:

$$1A + 1B \rightarrow 1C$$

Because A needs to collide with B to form C, the rate of formation of C is proportional to both the concentrations of A and B. Thus, we have the following relation, which is approximately true when the change in time, Δt, is very small. Since this is a rate, we see that the concentration of reactants and products change over a period of time.

$$\text{Rate} = \frac{\Delta[C]}{\Delta t} \approx k[A]^1[B]^1$$

Notice that the rate involves the change in concentration of C, $\Delta[C]$, over a period of time, Δt. The ratio of the two, is approximately equal to k, the rate constant for the reaction at a specific

Chapter 8: Kinetics and Equilibrium

temperature, multiplied by the concentrations of A and B, which are represented as [A] and [B]. The brackets, [ ], signify the concentration in molarity, or moles per liter, of the species that is inside the brackets, which is in this case, A and B. All of the compounds in the reaction are called species, because they exist simultaneously in solution during the reaction. The relation that was previously shown is only a rough approximation, because the concentration of A and B change over the course of the reaction. Thus, the relation is only precise when the change in time is infinitesimally small, so small that we are only looking at not much more than a single instant. To represent a very, very, very small change, we use d instead of Δ, just like what we previously did for the Clausius inequality. Thus, we have the following:

$$\text{Rate} = \frac{d[C]}{dt} = k[A]^1[B]^1$$

Since the reaction we are discussing proceeds to the right, the amount of C is increasing as the reaction occurs. When C is formed, a stoichiometric amount of A and B are consumed. Since $1A \rightleftharpoons 1C$, $1B \rightleftharpoons 1C$, and $1A \rightleftharpoons 1B$, we have the relation below:

$$\frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A]^1[B]^1$$

This is logical, since an increase in C, or a positive d[C], needs to consume A and B. Therefore, d[A] and d[B] would be negative, because the amount of A and the amount of B are decreasing as the reaction proceeds. Note, that in the case where volume does not change, the rate of change of amount of C, A, and B, are likewise related to each other through the following relation:

$$\frac{dC}{dt} = -\frac{dA}{dt} = -\frac{dB}{dt} = k[A]^1[B]^1 * V_{soln} = k_{new}[A][B], where\ k_{new} = k * V_{soln}$$

This just shows that concentrations can be converted into amounts if the volume of the solution is known. Although we can use amount, we usually work with concentrations because we can more easily scale up concentrations for convenience of calculation.

Chapter 8: Kinetics and Equilibrium

Uni-, Bi-, Ter-, and Poly- Molecular Reactions

But what happens when more than one molecule of a single type of reactant are needed? We again imagine the collisions required for reactions to proceed, in order to arrive at a reasonable explanation. Think about the three single-step reactions below:

$$Rxn_1 = A \rightarrow B + C$$

$$Rxn_2 = D + E \rightarrow F$$

$$Rxn_3 = G + H + I \rightarrow J + K$$
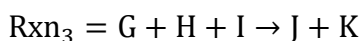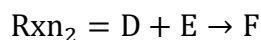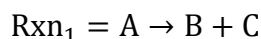
Unimolecular Reactions

Rxn_1 is called a unimolecular reaction. This means that one reactant is involved. You may wonder how this is possible, because there is nothing for the molecule A to collide with except for the walls of the reaction vessel, molecules of solvent, and other molecules of A. Remember when we discussed the density of electrons? Although we represent the bonds between atoms on a Lewis structure by placing two dots that represent the two electrons that contribute to the attraction, most of the time only 0.1 of an electron is present between the two atoms for a single bond, 0.2 of an electron is present between the two atoms for a double bond, and 0.3 of an electron is present between the two atoms for a triple bond. Thus, the electrons are not even present between the two atoms for most of the time, which allows for the disassociation of the molecule held together by the bond, especially when there is some agitation from a collision or from thermal energy in the form of translation, rotation, and vibration. However, note that although the electron density increases roughly proportionally to the number of bonds formed, the stabilization energies of multiple bonds are usually less than a multiple of the corresponding single bond. This is because the electrons repel each other, thus weakening the bond to the point where the strength is not close to the sum of the strengths of multiple single bonds, as was previously explained in the atomic structure section.

For most nonlabile substances, unimolecular reactions do not occur very frequently. However, many substances decompose, and a prominent example are the carbonates, which decompose when heated, as shown in the following unimolecular reaction. The Δ above the arrow indicates the forcing condition of high temperature.

Chapter 8: Kinetics and Equilibrium

Thermal Decomposition of $CaCO_3(s)$: $\quad CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$
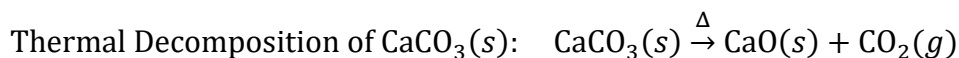
Because only one molecule is involved, the rate of Rxn_1 can be written as follows:

$$Rxn_1 = A \rightarrow B + C$$

$$Rate = -\frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A]$$

Note how a decrease in A, as represented by a negative d[A], corresponds to an increase in B and C, as represented by a positive d[B] and d[C] as the reaction proceeds. Another prominent similar reaction is the radioactive decay of many elements, where the fission of an atom leads to multiple products.

Bimolecular Reactions

Rxn_2 is called a bimolecular reaction.

$$Rxn_2 = D + E \rightarrow F$$
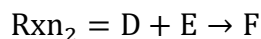
Note how in this case, D and E have to collide in order to form F. Thus, as expected, the rate law is of a familiar form:

$$Rate = \frac{d[F]}{dt} = -\frac{d[D]}{dt} = -\frac{d[E]}{dt} = k[D][E]$$

The formation of F depends on the presence of D as well as E.

Trimolecular Reactions

Rxn_3 is a trimolecular reaction (the word trimolecular is sometimes written as termolecular, because the prefixes tri- and ter- both mean 3). Although reactions involving three or more reactants can occur in a single step, the likelihood of collision is very low. However, if Rxn_3 proceeds in a single step, we have the following rate law:

$$Rxn_3 = G + H + I \rightarrow J + K$$

Chapter 8: Kinetics and Equilibrium
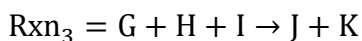
$$\text{Rate} = \frac{d[J]}{dt} = \frac{d[K]}{dt} = -\frac{d[G]}{dt} = -\frac{d[H]}{dt} = -\frac{d[I]}{dt} = k[G][H][I]$$

The reaction depends upon the collision of G, H, and I. Thus, the rate is proportional to the concentrations of G, H, and I.

When More Than One Molecule of a Species Are Needed in a Single Step Reaction

With this information, we can deduce the rate law for a reaction which involves multiple molecules of the same type, as seen in the reaction below:

$$Z + 2X \rightarrow Y$$

Looking at this equation, you can tell that Z has to simultaneously collide with 2X's in order for the reaction to proceed. Thus, the concentration of X is more important to the reaction than the concentration of Z, because the reaction depends on the simultaneous presence of 2X, but only 1Z. The process of figuring this out can be simplified by rewriting the equation.

$$Z + 2X \rightarrow Y \text{ is the same as } Z + X + X \rightarrow Y$$

Now you see it? The rate of the reaction is dependent on a single Z, but is dependent on two X's. Thus, the rate of the reaction is proportional to [Z], but twice proportional to [X]. Therefore, the rate is equal to a rate constant, k, multiplied by [Z], multiplied by [X], and multiplied by [X] again! Writing the rate law, we have the following:

$$\text{Rate} = \frac{d[Y]}{dt} = -\frac{1}{2}\frac{d[X]}{dt} = -\frac{d[Z]}{dt} = k[Z][X][X] = k[Z][X]^2$$

Note the -1/2 factor in front of the d[X]/dt. This is because the change in X is twice as much as the change in Y or the change in Z, because 1Y⇌2X⇌1Z. This is another trimolecular reaction, because three molecules must collide in order for this reaction to proceed.

Other Examples of Reactions Involving More Than One Molecule of a Species in a Single Step are Shown Below:

$$2W \rightarrow V$$

Chapter 8: Kinetics and Equilibrium
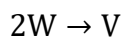
$$\text{Rate} = \frac{d[V]}{dt} = -\frac{1}{2}\frac{d[W]}{dt} = k[W]^2$$

Thus, we expect the rate of a single step reaction to be roughly equal to a constant multiplied by the concentration of the reagents that are involved in the reaction, raised to the power of their coefficients. Single step reactions are also called elementary steps. Experimental studies indeed prove this relationship.

Order of Reactions

Let us reexamine the previous reactions, in order to see if we can draw more insight on reaction rates in general.

Rxn₁ is a First Order Reaction:
$$\text{Rxn}_1 = A \rightarrow B + C$$

$$\text{Rate}_{\text{Rxn}_1} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = -\frac{d[A]}{dt} = k[A]^1$$

Here, we say that the reaction order is one, because the sum of the exponents of the concentrations in the rate equation is one, as shown as $[A]^1$.

Rxn₂ is a Second Order Reaction:
$$\text{Rxn}_2 = D + E \rightarrow F$$

$$\text{Rate}_{\text{Rxn}_2} = \frac{d[F]}{dt} = -\frac{d[D]}{dt} = -\frac{d[E]}{dt} = k[D]^1[E]^1$$

Here, we say that the reaction order is two, because the sum of the exponents of the concentrations in the rate equation is two, as shown as $[D]^1$ and $[E]^1$. Here another reaction of order 2:

$$2W \rightarrow V$$

$$\text{Rate} = \frac{d[V]}{dt} = -\frac{1}{2}\frac{d[W]}{dt} = k[W]^2$$

Chapter 8: Kinetics and Equilibrium
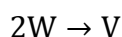
Rxn₃ is a Third Order Reaction:

$$Rxn_3 = G + H + I \rightarrow J + K$$

$$Rate_{Rxn_3} = \frac{d[J]}{dt} = \frac{d[K]}{dt} = -\frac{d[G]}{dt} = -\frac{d[H]}{dt} = -\frac{d[I]}{dt} = k[G][H][I]$$

Here, we say that the reaction order is three, because the sum of the exponents of the concentrations in the rate equation is three, as shown as $[G]^1$, $[H]^1$, and $[I]^1$.

Here is another reaction with an order of three, as the exponents 1+2 is equal to three.

$$Z + 2X \rightarrow Y$$
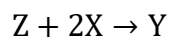
$$Rate = \frac{d[Y]}{dt} = -\frac{1}{2}\frac{d[X]}{dt} = -\frac{d[Z]}{dt} = k[Z][X][X] = k[Z][X]^2$$

Single-step reactions with order three and above are very unlikely, because they require the simultaneous collision of three or more molecules. However, they are possible if the concentrations of the reactants are very high, but the reactions are very unlikely to be useful due to low yields.

Finding Differential Rate Laws Using the Method of Initial Rates

To calculate the rate constant for a reaction, we measure the initial rate of the reaction when we perform the reaction with known concentrations, and then divide by the initial concentrations of the reactants raised to their respective powers.

Chapter 8: Kinetics and Equilibrium
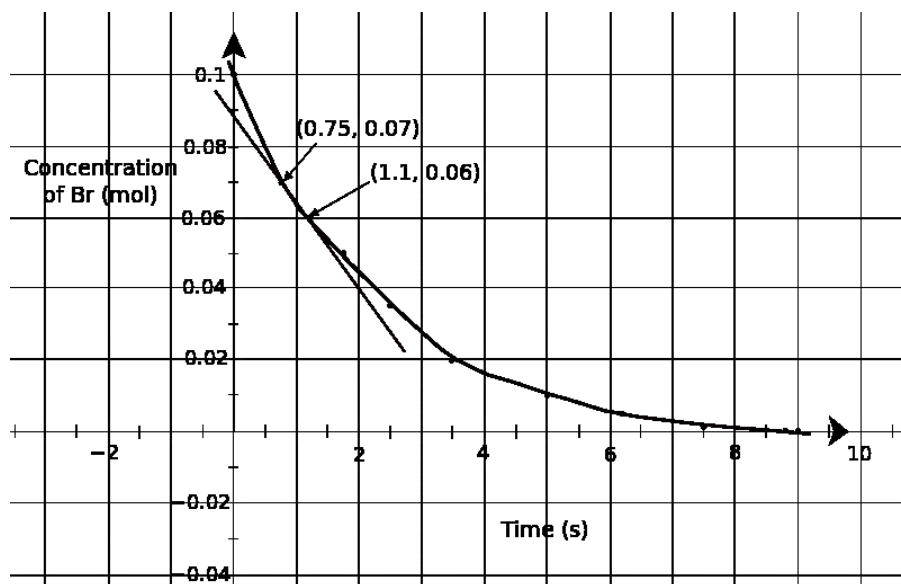
Figure 8.2. Rate laws can be found experimentally. Initial rates are found by plotting a concentration versus time graph, and we usually approximate the slope between two data points to be nearly equal to the initial change. Thus, the slope of the line, which is tangent to the concentration versus time curve, is approximately the initial rate.

We use initial rate, because it is the easiest to obtain, and also it is difficult to account for the concentrations when the reaction proceeds.
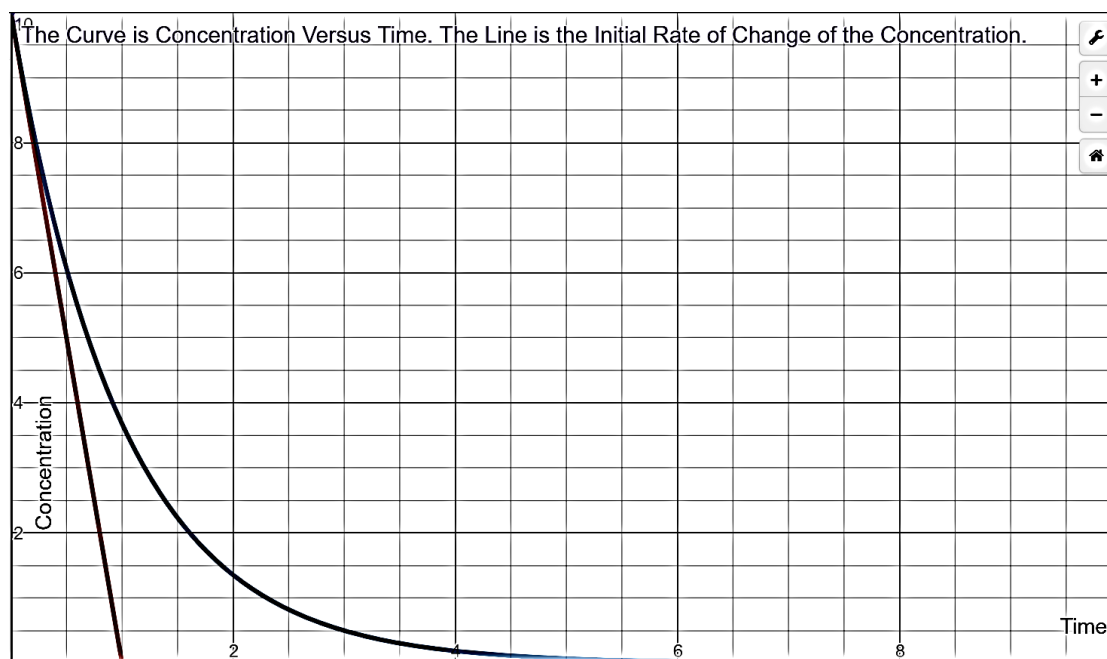
Figure 8.3. Of course, in the ideal situation, if we can find two data points very close to the beginning of the reaction, we can find a rate that is nearly equal to the actual initial rate, and our error would be very small. Here, the curve is the concentration versus time graph, and the slope of the line is the approximated initial rate.

217

Chapter 8: Kinetics and Equilibrium

For a First Order Reaction, We Do the Following:

$$Rxn_1 = A \rightarrow B + C$$

$$Rate_{Rxn_1} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = -\frac{d[A]}{dt} = k[A]^1$$

$$\frac{Rate_{i\ Rxn_1}}{[A]_i} = k$$

Any rate may be used, because the rate of consumption or production of a single species may be stoichiometrically used to find the rate of consumption or production of another species.

We Do the Same Process for a Second Order Reaction:

$$Rxn_2 = D + E \rightarrow F$$
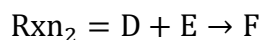
$$Rate_{Rxn_2} = \frac{d[F]}{dt} = -\frac{d[D]}{dt} = -\frac{d[E]}{dt} = k[D]^1[E]^1$$

$$\frac{Rate_{i\ Rxn_2}}{[D]_i[E]_i} = k$$

The easiest way to determine the rate constant is to perform the reaction with varying concentrations of the reagents while graphing the progress of the reactions. However, if we do not know the rate law, in order to determine the power that each reactant is raised to in the rate equation, we perform two trials for each reactant. In the two trials, only the concentration of one reactant is varied between the trials. All other reactants are used at the same high concentration in both trials. This method allows for fairly accurate determination of the order dependence the reaction has on the reactant that we are varying.

Use High Concentrations of All Reactants Except for the Varied

In both trials, all other reactants except for the one that we are varying are used at the same concentrations, and at high concentrations. This is because we do not want those reactants to vary in concentration. Equal concentration of all other reactants greatly simplifies calculations,

Chapter 8: Kinetics and Equilibrium

and the high concentration allows for the reaction to proceed without having any significant change in the concentration of all other reactants except for the reactant of interest. Thus, if the concentration of all other reactants except for the single reactant being varied are used in high concentrations, we can approximate their concentrations to be constant over the short period of time during which we measure the initial rate. This is known as Ostwald's method of swamping.

Verification of the Validity of the Swamping Approximation:
For example, a change of 0.0001 mole of a species has a far less significant effect on the concentration of that species for a 10 milliliter 10 molar solution than for a 10 milliliter 0.1 molar solution. We verify the validity of our approximation with the calculations below:

$$10 \text{ mL} * \frac{1 \text{ L}}{1000 \text{ mL}} * \frac{10 \text{ mol}}{1 \text{ L}} - 0.0001 \text{ mol} = 0.0999 \text{ moles}$$

$$\text{concentration} = \frac{\text{moles}}{\text{L}} = \left(.0999 \frac{\text{moles}}{10 \text{mL}}\right) * \frac{1000 \text{mL}}{\text{L}} = 9.99 \frac{\text{moles}}{\text{L}}$$

A change of 0.0001 mole corresponds to only a 0.1% change in concentration, for the 10 mL 10 molar solution.

Versus

$$10 \text{ mL} * \frac{1 \text{ L}}{1000 \text{ mL}} * \frac{0.1 \text{ mol}}{1 \text{ L}} - 0.0001 \text{ mol} = 0.0009 \text{ moles}$$

$$\left(0.0009 \frac{\text{moles}}{10 \text{mL}}\right) * \frac{1000 \text{ mL}}{\text{L}} = 0.09 \frac{\text{moles}}{\text{L}}$$

A change of 0.0001 mole corresponds to a 10% change in concentration, for the 10 mL 0.1 molar solution.

A Hypothetical Experiment

Let us walk through a hypothetical experiment. In a single step reaction, X and Y are consumed to form Z. However, we do not know the powers that X and Y are raised to in the rate expression, nor the rate constant. Thus, we have the following:

$$\text{Rate} = k[X]^m[Y]^n, \text{where } k, m, \text{ and } n \text{ are unknown}$$

Chapter 8: Kinetics and Equilibrium

To find k, m, and n, we need to perform two experiments for each reactant. Thus, we need four trials in this case. We begin with varying the concentration of Y, and using a constant initial high concentration of X. Thus, the rate equation is approximately equal to the rate constant multiplied by the initial concentration of X raised to its respective power, multiplied by the concentration of Y, raised to its respective power.

$$\text{Rate} = k[X]^m[Y]^n \approx k[X]_i^m[Y]^n$$

In this reaction, m and n are called the partial orders of the reaction, and $m+n$ is called the overall or global order of the reaction. Note that because X is relatively constant during the small range of time that we conduct the experiment in, we can approximate the concentration of X to be the same as the initial concentration of X. Note how the initial concentration of X is a constant, and does not change as the reaction proceeds, because it is set at the beginning of the experiment! Simplifying even further, we can create a pseudo rate constant, $k^\sim$, which is equal to k multiplied by the initial concentration of X raised to its respective power.

$$\text{Rate} \approx k^\sim[Y]^n, \text{where } k^\sim = k[X]_i^m$$

Since X does not change significantly, and the initial concentration of X is kept constant over the two trials, the rate of reaction in this case will vary only due to the differences in concentration of Y. Thus, the reaction is said to be pseudo-nth order with respect to Y, because if only Y is varied, the reaction behaves as if it was a nth-order reaction. Although any two different concentrations of Y can be used, in order to simplify calculations, it is preferred to choose the initial concentrations of Y for the two trials to be multiples of each other. If we do not know n, and when the reaction follows the rate law Rate $\approx k^\sim[Y]^n$, then the n can be found as follows. If we divide the two rates for the two trials, we get the following relation:

Relation Between Rates to Determine Order:
$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k^\sim[Y]_{1i}^n}{k^\sim[Y]_{2i}^n} = \frac{[Y]_{1i}^n}{[Y]_{2i}^n}$$

Because for fractions, $\frac{a^m}{b^m} = \left(\frac{a}{b}\right)^m$, we can rewrite the result to find the following useful formula:

$$\frac{\text{Rate}_{1i}}{\text{Rate}_{2i}} = \left(\frac{[Y]_{1i}}{[Y]_{2i}}\right)^n$$, where n is the power that Y is raised to in the rate equation.

Chapter 8: Kinetics and Equilibrium

Analysis of Experimental Initial Rates and Initial Concentrations to Find the Rate Constant and the Order of Reaction

Thus, using the relation above, and analyzing our initial rates and our initial concentrations, we can find n. For example, if we double the initial concentration of Y for experiment 2 and we observe that the initial rate for experiment 2 is double the initial rate of experiment 1, then n is 1, and we observe a linear relationship between [Y] and the reaction rate. If we double the initial concentration of Y for experiment 2 and we observe that the initial rate for experiment 2 is 2^2 times the initial rate of experiment 1, then n is 2, and we observe a square relationship between [Y] and the reaction rate. It follows that for n=3, if we double [Y], the rate is multiplied by 2^3, and so forth. It follows that if we multiply the initial concentration of Y by any factor b, then for a first order reaction with respect to Y, the rate is multiplied by b^1, for a second order reaction with respect to Y, the rate is multiplied by b^2, and so forth. If we change the initial concentration [Y], and we do not observe any change in rate, then the reaction is said to be zeroth-order with respect to [Y], and n is equal to zero. Doing the same process for X allows for us to find the power, m, that [X] is raised to. Thus, we arrive at the following rate law:

$$\text{Rate} = k[X]^m[Y]^n, \text{where } m \text{ and } n \text{ are known.}$$

The only thing left unknown, is the rate constant itself. Using any trial from the experiment, we can find the rate constant, by simply dividing.

$$\text{Initial Rate} = k[X]_i^m[Y]_i^n, \text{where } i \text{ denotes initial, and } m \text{ and } n \text{ are known}$$

$$\frac{\text{Initial Rate}}{[X]_i^m[Y]_i^n} = k$$

Thus, we just deduced the rate law for the experiment, and can find the rate of the reaction for other circumstances!

The Pseudo Rate Law and Constant, and Ostwald's Method of Swamping

During the experiment, we found the pseudo rate constant, and the pseudo rate law. Although we did not discuss zeroth order reactions, where the reaction occurs relatively

Chapter 8: Kinetics and Equilibrium

independently of the concentration of the reactants, we will do so now. We first begin with the second order reaction that we are familiar with:

$$Rxn = X + Y \rightarrow Z$$
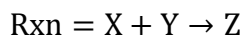
$$\text{Rate Law} = k[X][Y]$$

If we begin with a high concentration of X, and vary the concentration of Y, we can say that the reaction is swamped. The method is also called Wilhelm Ostwald's method of flooding, or the method of isolation, or swamping, as flooding the reaction with X allows for us to isolate the effects of Y on the reaction. Thus, the high excess of X means that there is very little variation in the concentration of X, and that the reaction will appear to be dependent solely on Y. Thus, the pseudo rate law can be written as follows:

$$\text{Rate} \approx k^{\tilde{}}[Y], \text{where } k^{\tilde{}} = k[X]_i$$

For this reaction, we say that it is a pseudo first order reaction, because it is first order with respect to Y. Thus, swamping one reactant allows for the rate law to be expressed in terms of a pseudo rate constant, and the concentration of the remaining reactants.

Zeroth Order Differential Rate Law

There are very few reactions in nature that follow zero order kinetics, where the rate of reaction is independent of the concentration of the reactant. However, when reactions are observed to be zeroth order, they may be in reality just reactions that are swamped. We have already seen with the second order reaction, where swamping allows for the observation of first order kinetics in a reaction that is second order. Thus, if we swamp a reaction, especially in the presence of a catalyst, we have the following:

$$W + Z \rightarrow W + X + Y$$

$$\text{Rate} = k[W][Z]$$

We know that W is a catalyst, as it is regenerated in the reaction, and the reaction possibly will not occur at an appreciable rate without W. Typically, the presence of a catalyst such as an enzyme may speed up a reaction anywhere from a thousand to several million times,

Chapter 8: Kinetics and Equilibrium

with respect to the rate of reaction in the absence of the catalyst. Thus, the reaction is unlikely without the catalyst. Most catalysts have active sites that allow for the reaction to bypass the normally higher activation energy by providing an alternative pathway. When the concentrations of reactants are very high, the active sites may be saturated. No matter how much more reactant we add, since the reaction is already proceeding at maximum possible speed due to the saturation of the catalyst, we would not observe any increase in rate. Often, in a reaction, we use the word "substrate" to indicate the reactant that we are starting with. The K_M is the concentration at which the reaction rate is half of its theoretical value, which is sometimes desirable to know, especially when dealing with enzyme-based catalysis.
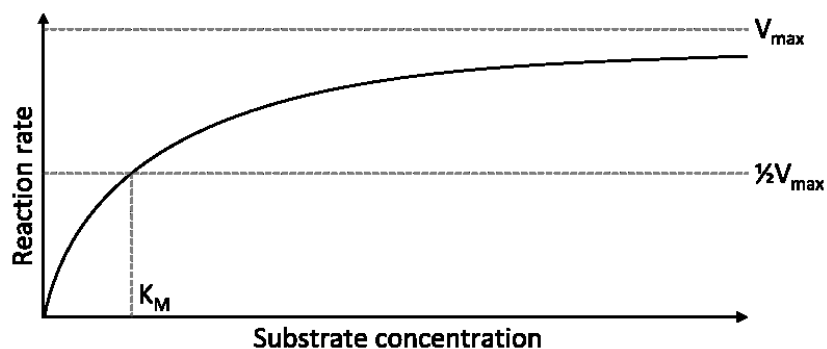
Figure 8.4. Here, it shows that for reactions which require a catalyst to proceed, the rate approaches an ideal maximum value as the concentration of the reactant (also called substrate) is increased. Thus, at high concentrations of reactant, an increase in concentration of reactant does not lead to a significant increase in reaction rate.

For the reaction above at high concentrations of Z, we observe the following:

$$\text{Rate} = k^\sigma[\text{W}]$$

Where Z no longer appears in the rate equation, because the concentration of Z is higher than necessary to ensure that nearly all of the active sites of the catalyst are occupied at all times.

Note, however, that more of the catalyst does speed up the reaction. Thus, when Z is at very high concentrations, we observe that the reaction appears to be zeroth order with respect to Z. If W does not change, then the rate is fixed, and is simply equal to a constant.

$$\text{Rate} = k[\text{Z}]^{\text{Zeroth Order}} = k$$

Chapter 8: Kinetics and Equilibrium

For this type of reaction, we say that it is zeroth order, because the power of all of the concentrations of the reactants is equal to 0, thus the rate is a constant multiplied by 1, which is just the constant itself.

Units of the Rate Constant

Depending on the order of reaction, the rate constant has different units. Although usually teachers ask you to memorize the units, that is unnecessary. A quick trick is to just derive the units using dimensional analysis.

For a Zeroth Order Reaction, We Have the Following:

$$\text{Rate} = \frac{d[A]}{dt} = k, \text{where A is some species}$$

Rate, which is equal to the change in the concentration of some species over the change in time, is in moles per liter per second. Thus, since the rate is equal to the constant itself for a zeroth order reaction, the units of the constant is simply moles per liter per second, or

$$\frac{\text{mol}}{\text{L} * \text{s}} = \text{mol} * \text{L}^{-1}\text{s}^{-1}$$

For a First Order Reaction:

$$\text{Rate} = \frac{d[A]}{dt} = k[B], \text{where A is some product, and B is some reactant}$$

Here, the rate, which is in moles per liter per second, is equal to the constant multiplied by a concentration. Since we are using molarity, concentration has the units of moles per liter, or molar. Dimensional analysis brings us to the following conclusion:

$$\text{Rate} = \frac{d[A]}{dt} = k[B]$$

$$\frac{\text{mol}}{\text{L} * \text{s}} = \frac{\text{mol}}{\text{L} * \text{s}} = (\text{units of } k)\left(\frac{\text{mol}}{\text{L}}\right)$$

Chapter 8: Kinetics and Equilibrium

$$\text{units of } k = \frac{\left(\frac{\text{mol}}{\text{L} * \text{s}}\right)}{\left(\frac{\text{mol}}{\text{L}}\right)} = \frac{1}{\text{s}} = \text{s}^{-1}$$

For a Second Order Reaction:

$$\text{Rate} = \frac{d[A]}{dt} = k[B][C], \text{ where } [A] \text{ is some product, and } [B] \text{ and } [C] \text{ are reactants}$$

$$\frac{\text{mol}}{\text{L} * \text{s}} = \frac{\text{mol}}{\text{L} * \text{s}} = (\text{units of } k) \left(\frac{\text{mol}}{\text{L}}\right) \left(\frac{\text{mol}}{\text{L}}\right)$$

$$\text{units of } k = \frac{\text{L}}{\text{mol} * \text{s}} = \text{L} * \text{mol}^{-1} * \text{s}^{-1}$$

General Equation for Units of the Rate Constant

As we continue, we observe that the general trend is the following, where m is the global order of the reaction (the global order of the reaction is equal to the sum of all partial orders of the reactants):

$$\text{Units of } k = \frac{\left(\frac{\text{mol}}{\text{L} * \text{s}}\right)}{\left(\frac{\text{mol}}{\text{L}}\right)^m}, \text{ where } m \text{ is the overall global order of the reaction.}$$

Expressing the Rate Constant in Pressures

The rate constant, for reactions in the gas phase, can also be expressed in pressures. Theoretically, for ideal gases, the concentration, $\frac{n}{V}$, is equal to $\frac{p}{RT}$.

$$\frac{p}{RT} = \frac{n}{V}$$

$$p = \frac{n}{V} * RT$$

Therefore, if the presence of solvent molecules and other species do not affect the rate of reaction, the reaction rate can be expressed as the previous rate constant, divided by RT raised to

Chapter 8: Kinetics and Equilibrium

the global order of the reaction, multiplied by the pressures of the species raised to their respective powers.

$$\text{Rate} = k[\text{X}]^m[\text{Y}]^n = \frac{k}{(RT)^{m+n}}([\text{X}]RT)^m([\text{Y}]RT)^n$$

And, if we define another k, which we'll just call k_p, that is based upon pressures, we can rewrite the rate as follows:

$$\text{Rate} = k_p(p_\text{X})^m(p_\text{Y})^n, \text{where } k_p = \frac{k}{(RT)^{m+n}},$$

and p_X and p_y are the partial pressures of X and Y

Note that this is only in the case of ideal gases. For real gases, the rate constant must be experimentally determined.

Equilibrium, and Berthollet's Hypothesis

The study of equilibrium began with the realization that chemical reactions stabilize at some point, and curiously enough, most reactions do not go to completion. That means that not all of the reactants react, and the yield is lower than the theoretical ideal. Reactions are only useful if the yield is sufficiently high, because low yields lead to wastage of materials. In 1803, Claude Louis Berthollet proposed the concept of chemical equilibrium to explain why reactions do not go to completion. He proposed that at a certain temperature, the concentrations of reacting substances always reach a constant ratio of concentrations of products and reactants raised to their stoichiometric constants. Although the law holds precisely for concentration only when the concentrations of the reactants and products are very low, for the most part using concentrations or pressures to approximate is a fairly valid technique that simplifies calculations. However, remember that when there is a high concentration of a species, there will be large observed deviations from the approximation that we make when calculating the equilibrium and rate constants using concentration and pressure instead of activity and fugacity.

Chapter 8: Kinetics and Equilibrium

The Equilibrium Constant, From the Law of Mass Action

Most reactions do not go to completion. Rather, the ratio of the products and the reactants always reach towards some point, which we call "equilibrium." However, the reaction does not simply stop. Rather, since most reactions can proceed in both directions, the system reaches a dynamic equilibrium, when the same amount of reactants and products are simultaneously produced and consumed. That occurs when both forward and reverse reactions occur constantly at the same rate without ceasing. Thus, the concentration of the species present does not change. We can illustrate this concept using the following, which was proposed by Cato Maximilian Guldberg and Peter Waage in their 1864 papers "Studies Concerning Affinity" (Waage and Guldberg), "Experiments for Determining the Affinity Law" (Waage), and "Concerning the Laws of Chemical Affinity" (Guldberg). In their time, the term affinity just meant how chemically favorable it is for a reaction to occur. Thus, the following is called the Law of Mass Action (LMA), as it is the result of a very large number of microscopic interactions that work together to stabilize the system at equilibrium:

$$\text{Single step reaction:} \, \alpha A + \beta B + \cdots \rightleftharpoons \omega Z + \psi Y + \cdots$$
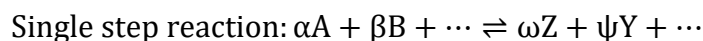
$$\text{Rate of forward reaction} = k_f [A]^\alpha * [B]^\beta * \ldots$$

$$\text{Rate of reverse reaction} = k_r [Z]^\omega * [Y]^\psi * \ldots$$

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[Z]}{dt} = \frac{d[Y]}{dt} = 0 \text{ at equilibrium}$$

Because the concentrations of the species are not changing, the rate of the forward and the reverse reactions are equal. Therefore, we have:

$$k_f [A]^\alpha * [B]^\beta * \ldots = k_r [Z]^\omega * [Y]^\psi * \ldots$$

Using this relation, we can find the ratio of the rate constants of the forward and reverse reactions:

$$\frac{k_f}{k_r} = \frac{[Z]^\omega * [Y]^\psi * \ldots}{[A]^\alpha * [B]^\beta * \ldots}$$

Chapter 8: Kinetics and Equilibrium

We define the equilibrium constant to be equal to the ratio of the forward and reverse rate constants, and define the concentrations of products and reactants that satisfy the equilibrium constant the equilibrium concentrations for the reaction at a given temperature.

$$\frac{k_f}{k_r} = K, \text{where } K \text{ is the equilibrium constant}$$

When the equilibrium constant is expressed in concentration, we can also write it as K_c, and when the equilibrium constant is expressed in pressures, we can also write it as K_p.

Pure Solids and Liquids are Never Included in the Rate nor the Equilibrium Expression

Pure solids and liquids are never included in the rate expression nor the equilibrium constant expression, because pure solids and liquids have fairly constant concentrations that do not change as the reaction proceeds. They are simply factored into the corresponding rate or equilibrium constant, which are experimentally determined anyway. As long as the pure liquid or solid is present, then equilibrium may be achieved. Also, substances that do not participate in the reaction are not included either, because they are mostly irrelevant to the reaction at hand.

Standardization

Usually, to make thermodynamic calculations easier, the equilibrium constant and the rate constant are expressed relative to their standard states. Standard Temperature and Pressure (STP), indicated by a superscripted plimsoll, $\ominus$, is at 273.15 K and 1 bar=10^5 Pa. Standard Ambient Temperature and Pressure (SATP), indicated by a degree symbol, °, is at 298.15 K and 1 atmosphere. Since water freezes at 273.15 K, for reactants in solution, the standard reference state is when the concentration is 1 molar, and the temperature is 298.15 K. Most tables of reference thermodynamic quantities are catalogued at SATP. Likewise, for most reactions in gaseous state, the standard is 1 atmosphere of pressure at 298.15 K. The standardization can be done for most dilute solutions by simply dividing the concentrations of the reactants by 1 molar before raising the species to the corresponding power. Thus, we do the following for reactions in solution:

Chapter 8: Kinetics and Equilibrium

$$\text{Single step reaction: } \alpha A + \beta B + \cdots \rightleftharpoons \omega Z + \psi Y + \cdots$$

$$\text{Rate of forward reaction} = k_{sf} \left(\frac{[A]}{1 \text{ Molar}} \right)^{\alpha} * \left(\frac{[B]}{1 \text{ Molar}} \right)^{\beta} * \cdots$$

$$\text{Rate of reverse reaction} = k_{sr} \left(\frac{[Z]}{1 \text{ Molar}} \right)^{\omega} * \left(\frac{[Y]}{1 \text{ Molar}} \right)^{\psi} * \cdots$$

The only difference observed is that we just divided out the units associated with concentration. When the reactants are in gaseous form, as seen before, the reaction rate can also be expressed in terms of the pressure of each individual gas, and these pressures can also be standardized by dividing by $P°$, which is 1 atmosphere of the gas at 298.15 K, and the rate law can be rewritten either in terms of a new constant, or in terms of another constant multiplied by a constant, because constants multiplied by constants are still constants.

For an Ideal Gas, the Following Holds, Because Pressure is Related to Concentration Through the Ideal Gas Law:

$$p = \frac{n}{V} RT = \text{concentration} * RT$$

$$\text{Rate} = k[X]^m[Y]^n = k \left(\frac{[X]}{1 \text{ Molar}} \right)^m \left(\frac{[Y]}{1 \text{ Molar}} \right)^n * \cdots = \frac{k}{(RT)^{m+n+\cdots}} ([X]RT)^m ([Y]RT)^n * \cdots$$

$$= k_p \left(\frac{[X]RT}{1 \text{ Molar} * RT} \right)^m \left(\frac{[Y]RT}{1 \text{ Molar} * RT} \right)^n * \cdots = k_p \left(\frac{p_X}{P°} \right)^m \left(\frac{p_Y}{P°} \right)^n * \cdots$$

$$= k_p (p_X)^m (p_Y)^n * \cdots$$

Where $k_p = \dfrac{k}{(RT)^{m+n+\cdots}}$ for ideal gases, $P° = $ the standard ambient pressure of 1 atm,

$$p_X, p_Y, \text{etc. are the partial pressures of X, Y, Z, etc,} \quad R = 0.0821 \frac{L * atm}{mol * K}$$

However, note that for non-ideal real gases, using the ideal gas approximation is only a rough approximation, and the new constant must be experimentally determined.

Chapter 8: Kinetics and Equilibrium

K is Unitless

Although specifying units of concentration and pressure might not seem to be useful for rates, as nearly nothing changes, it is very useful for relating equilibrium constants and thermodynamic properties, because we use different tables for thermodynamic properties depending on whether we are using a standard of 1 molar in solution, or 1 atmosphere of pressure in air, at 298.15 K. Thus, for equilibria which are relative to 1 molar concentration, the K_c would involve molarity, whereas for equilibria which are relative to 1 atmosphere, the equilibrium constant K_p would involve pressure. For the equilibrium constant, we have:

$$K_c = \frac{k_f}{k_r} = \frac{\left(\frac{[Z]}{1 \text{ Molar}}\right)^\omega * \left(\frac{[Y]}{1 \text{ Molar}}\right)^\psi * \cdots}{\left(\frac{[A]}{1 \text{ Molar}}\right)^\alpha * \left(\frac{[B]}{1 \text{ Molar}}\right)^\beta * \cdots}$$

Note that K is a unitless number, because of the fact that the units of concentration are divided out when we standardize. This is preferred for thermodynamic calculations.

Writing an Expression for the Equilibrium Constant of a Balanced Reaction

According to the law of mass action, to find an equilibrium constant of a generic chemical reaction, we do the following.

First, We Write the Balanced Equation:
$$\text{Reaction: } \alpha A + \beta B + \gamma C + \cdots \rightleftharpoons \omega Z + \psi Y + \cdots$$

Where A, B, C, Z, Y, etc. are the individual molecules called "species" that participate in the reaction, and α, β, γ, ω, ψ, etc. are the coefficients in the balanced equation for the corresponding species.

Chapter 8: Kinetics and Equilibrium

For K_c, in Terms of Concentrations:
　　Then, as we seen before, we place the product species raised to their respective
coefficients on the numerator, and place the reactant species raised to their respective
coefficients on the denominator as follows:

$$K_c = \frac{[Z]^\omega [Y]^\psi * \cdots}{[A]^\alpha [B]^\beta [C]^\gamma * \cdots}$$

The [ ] indicate concentration, which usually is measured in $\frac{\text{mol}}{\text{L}}$, or molarity. Note that the
coefficients are not multiplied to the species, but rather expressed as powers. This is from the law
of mass action, and allows for us to calculate the equilibrium constant. Once we know the
equilibrium constant, we can use the equation to calculate equilibrium concentrations and
pressures.

For K_p, in terms of Pressures:
　　We simply express the species in terms of their partial or absolute pressures. The reason
why we can use either is because the partial pressure is just equal to the absolute pressure
divided by a total pressure, which cancels out the units but leaves the numerical values intact.
The equilibrium constant may also be expressed in terms of pressure. We begin with the law of
mass action.

Generic Single Step Reaction: $\alpha A + \beta B + \gamma C + \cdots \rightleftharpoons \omega Z + \psi Y + \cdots$

At equilibrium, $k_{pf} = (p_A)^\alpha (p_B)^\beta * \cdots$ is equal to $k_{pr} = (p_Z)^\omega (p_Y)^\psi$

We define $K_p = \dfrac{k_{pf}}{k_{pr}}$

Therefore, $K_p = \dfrac{k_{pf}}{k_{pr}} = \dfrac{(p_Z)^\omega (p_Y)^\psi * \cdots}{(p_A)^\alpha (p_B)^\beta (p_c)^\gamma * \cdots}$

Conversion for Ideal Gases

　　Sometimes, we convert between equilibrium constant expressions by applying a gas law.
Usually, the example would be given in a way that suggests for you to apply the ideal gas law in

Chapter 8: Kinetics and Equilibrium

order to approximate pressures. For example, if we apply it to the equilibrium constant above, we can convert the concentrations into pressures, as follows:

$$pV = nRT \rightarrow p = nRT/V$$

$$\frac{n_{\text{species}}}{V_{\text{of reaction vessel}}} = \text{concentration of species} = \text{Molarity of species} = [\text{species}]$$

$$p_{\text{species}} = [\text{species}]RT$$

When we substitute in, we find that the pressure equilibrium constant is just equal to the concentration equilibrium constant times $(RT)^{\Delta n}$, where R is the molar gas constant from the ideal gas law, T is the temperature in kelvin, and Δn is equal to the change in number of moles of gas. Be sure to use the thermodynamic absolute scale in kelvins for temperature, because the ideal gas law depends on the thermodynamic absolute ideal gas temperature scale, and also the equilibrium constant is a thermodynamic quantity.

$$K_c = \frac{k_f}{k_r} = \frac{[Z]^{\omega}[Y]^{\psi} * \ldots}{[A]^{\alpha}[B]^{\beta}[C]^{\gamma} * \ldots}$$

$$K_p = \frac{k_{pf}}{k_{pr}} = \frac{(p_Z)^{\omega}(p_Y)^{\psi} * \ldots}{(p_A)^{\alpha}(p_B)^{\beta}(p_C)^{\gamma} * \ldots}$$

$$Where\ k_{pX} = \frac{k}{(RT)^X}, \text{where } X \text{ is the sum of the exponents, and } p_s$$

$$= [s]RT, \text{where s is an arbitrary species that follows the ideal gas law.}$$

Thus, applying rules of exponents, we have the following relation for ideal gases:

$$K_p = K_c * (RT)^{[\omega+\psi+\cdots]-[\alpha+\beta+\cdots]} = K_c * (RT)^{\Delta n},$$

where Δn is the change in number of moles of gas for reaction.

$$R = 0.08314 \text{ L} * \frac{\text{bar}}{(\text{mol}^{-1})(\text{K}^{-1})}$$

Again, this is consistent with the law of mass action. However, for nonideal gases, the relation does not hold, and we only have the result from the law of mass action, where K_p needs to be determined experimentally.

Chapter 8: Kinetics and Equilibrium

Example of the Haber Bosch Process

Thus, for the balanced thermochemical equation that follows, which is the classical favorite example of the Haber Bosch process, we have the following:

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) + 92.4\frac{kJ}{mol}, T = 745 \text{ K, Fe Cat.}, p \approx 25{,}500 \text{ kPa}$$
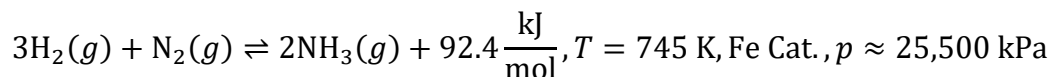
Note that the amount of energy involved in the reaction and the temperature at which the reaction occurs are important. This is because equilibrium is primarily dependent on thermodynamic properties of the reactants and products, and does not concern itself with the intermediates. However, do note that if there is no reaction, equilibrium can take nearly forever to reach, as in the example of the metastable diamond. The equilibrium constant for the Haber-Bosch reaction is as follows:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.118 \text{ , Haber Bosch Process}, T = 745 \text{ K}$$

Thus, hydrogen gas, nitrogen gas, and ammonia gas are the species that are present in this reaction, and the 3, 2, and 1 (above the N_2, but not shown) are the coefficients of the species which they are raising to a power. For pressure, we use the following:

$$K_p = \frac{\left(p_{NH_3}\right)^2}{\left(p_{N_2}\right)\left(p_{H_2}\right)^3}$$

If we assume ideal gas behavior, we can convert between the two constants as follows:

$$K_p = K_c * (RT)^{\Delta n} = \frac{[NH_3]^2}{[N_2][H_2]^3} * (RT)^{\Delta n} = \frac{[NH_3]^2}{[N_2][H_2]^3} * (0.082057 * 745)^{-2}$$

$$= 3.16 * 10^{-5} \text{ , Haber Bosch Process}, T = 745 \text{ K}$$

However, since the reaction is occurring at such high pressures, we expect a large amount of error for this approximation.

Chapter 8: Kinetics and Equilibrium

Integrated Rate Laws

Zeroth Order Reactions

For a zeroth order reaction, the rate is simply equal to the rate constant. Thus, for the following reaction, when catalyst W is kept constant, and there is a large concentration of Z, we observe zeroth order kinetics. For the following example, we will discuss Z and X. However, likewise, we could also discuss Y, but we will not do so, because it can just be related stoichiometrically to Z and X. Very often, for a rate law, if we know the balanced equation, we could just be given a single rate, and very easily obtain the other rates through stoichiometry. The following, which we have seen before, is our zeroth order reaction:

$$W + Z \rightarrow W + X + Y$$

$$\text{Rate} = \frac{d[X]}{dt} = \frac{d[Y]}{dt} = k, \text{where } k \text{ is some constant}$$

Because this rate law is based upon a difference, as symbolized by the d preceding the concentration of X and the time, t, this form of a rate law is called a differential rate law. Although this form is useful to find the rate constant based upon an initial rate of change, it is not very useful for finding the amount of X produced in a certain amount of time. Thus, we need something called the integrated rate law. Usually, the differential rate law is written as an expression of the reactants, but for a zeroth order reaction, it does not matter, as the rate law is a constant, and is independent of the concentration of a species. Alternatively, we could have also written $d[Z] = -kdt$. Note that for [X] there is no negative, because X is being formed. Thus, [X] increases over time. Z, however, is being consumed. Thus, [Z] decreases over time.

Now, we integrate, to obtain our integrated rate law. To integrate means to put together. Thus, when we integrate, we add together all the little changes in the concentration of X. Rewriting the rate law above, we can get the following:

$$d[X] = kdt$$

Here, a little change in the concentration of X during a little period of time, d[X], is equal to k multiplied by that little change in time, dt. Thus, to find what the little changes in [X] equal, we sum them together. To do this type of summing, we draw a big S, which looks like this: $\int$. What this S means is to just add up all the little pieces of whatever that comes after it. Thus, adding up

Chapter 8: Kinetics and Equilibrium

all the little changes in [X], or adding up all of the d[X]'s, we get a significantly large change in [X], or Δ[X]. Δ[X] simply means to take the final concentration of X, $[X]_f$, and subtract from $[X]_f$ the initial concentration of X, $[X]_i$. When the big S, written as $\int$, has an i written at its bottom and a f written at its top, it simply means to find the change between the initial and final states of the system. Thus, we get the following:

$$\int_i^f d[X] = \Delta[X] = [X]_f - [X]_i$$

And, doing the same to the opposite side,

$$\int_i^f k dt = k \int_i^f dt = k\Delta t = k(t_f - t_i)$$

Note how we can take the k outside of the sum, and multiply it to the change in time after we sum up all of the small changes in time. That is because the k is a constant, and all it does is multiply the change in time to relate the change in time to the change in the concentration of [X]. Just like how if we add two equations together, we still have an equation, the two sides of the rate law are still equal after we sum up the small changes of each side. Thus, we have:

$$[X]_f - [X]_i = k\Delta t$$

Thus, the final concentration of X formed after a period of time Δt can be found as follows:

$$[X]_f = [X]_i + k\Delta t$$

Note how the concentration of X is being added to, as time passes. This is because X is being produced as the reaction proceeds. Since 1 X is stoichiometrically equivalent to 1 Z, where an increase in X equals a corresponding decrease in Z, we can also write the change in concentration in Z as follows:

$$[Z]_f = [Z]_i - k\Delta t$$

which we would have obtained if we integrated the other expression, $d[Z] = -k dt$. Note that here the concentration of Z is being subtracted from as time passes. This is because Z is being consumed as time passes.

Chapter 8: Kinetics and Equilibrium

Half-Life

For many reactions, the half-life is a quantity that is tabulated. For zeroth order reactions, the half-life, or when reactant Z reaches half of its original concentration, can be found by substituting in $\frac{[Z]_i}{2}$ for $[Z]_f$. Thus, we have:

$$\frac{[Z]_i}{2} = [Z]_i - k\Delta t$$

We want time, because life is measured in units of time. Thus, we solve for Δt.

$$t_{\frac{1}{2}} = \frac{[Z]_i}{2k}$$

What this really tells us is that the amount of time that is necessary for the reaction to be half done is the initial concentration of our reactant, divided by 2, and then divided by our rate constant, for a zeroth order reactant. We also notice for a zeroth order reaction, that when we multiply the half-life time by two and substitute it into the integrated rate law, we get zero. That means that the reaction goes to completion in two half-lives for a zeroth order reaction.

$$0 = [Z]_i - k\left(2 * t_{\frac{1}{2}}\right) = [Z]_i - k\frac{2[Z]_i}{2k} = [Z]_i - [Z]_i$$

Likewise, when half of Z has been consumed, it produces a stoichiometrically equivalent amount of X.

Plotting a Line

For the zeroth order reaction, the integrated rate law is in the form *y=b-mx*, which is the form of a line with a positive y intercept, and negative slope.

$$[Z]_f = [Z]_i - k\Delta t$$
$$y = b - mx$$

If we plotted $[Z]$ versus Δt, then we would get a straight line, with a slope of *-k*, a y-intercept of $[Z]_i$, and an x-intercept of $2t_{\frac{1}{2}}$. What this means, is that we start with an initial concentration of

Chapter 8: Kinetics and Equilibrium

Z, $[Z]_i$, the amount of Z decreases at a constant rate, k, and we run out of Z in two half-lives. Also, after two half-lives, all the X that can be possibly formed are formed, and the graph of $[X]$ versus t is a straight line beginning at $[X]_i$, which eventually becomes a horizontal line when all the Z runs out, and the amount of X stops increasing.
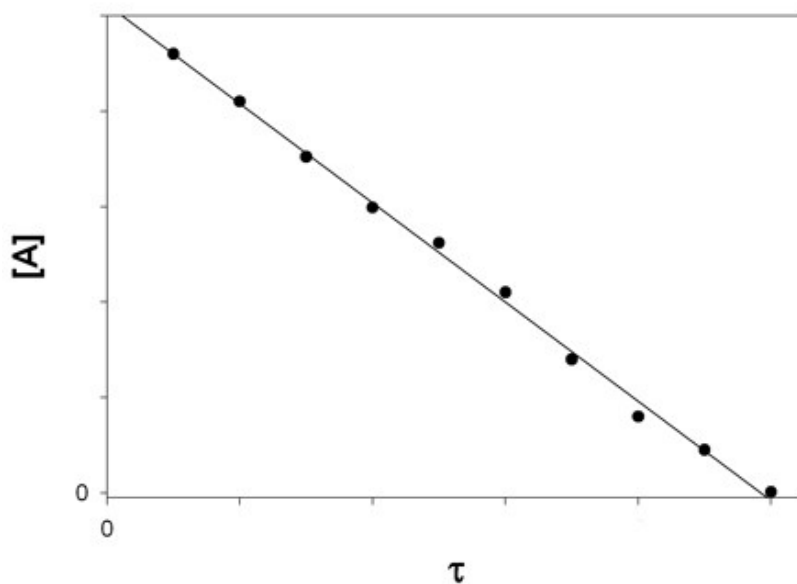
Figure 8.5. For a zeroth order reaction, the concentration of the reactant versus time is a straight line. One half of the reactant is consumed by the half-life, and no reactant remains after two half-lives. Note that the first order reaction is the only reaction to go to completion.

Note for Pseudo Zeroth Order Reactions:
However, note that for a pseudo zeroth order reaction, as above, the reaction will fail to follow the zeroth order kinetics when the concentration of reactant Z is too low to saturate the catalyst W. Then, when enough Z has been consumed, the rate law would change from pseudo zeroth order to first order, because although the catalyst changes the rate, it does not count as a reactant nor a product, and does not appear in the rate law, although its effects are multiplied into the rate constant for the catalyzed reaction.

First Order Reactions
For a first order reaction with respect to the reactant A, we have the following:

Chapter 8: Kinetics and Equilibrium

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]$$

Likewise, we separate the d[A] and the dt, and move everything with an A to one side.

$$-d[A] = k[A]dt$$

$$\frac{d[A]}{[A]} = -kdt$$

We have a rule for summing up something of the form $\frac{d[A]}{[A]}$, which is: $\int_i^f \frac{d[A]}{[A]} = \Delta \ln[A]$. This rule is proved in the mathematics appendix. Summing the results of both sides, we get:

$$\Delta \ln[A] = \ln[A]_f - \ln[A]_i = -k\Delta t$$

Thus, the integrated rate law, is equal to:

$$\ln[A]_f = \ln[A]_i - k\Delta t$$

Half-Life of a First Order Reaction is a Constant

For first order reactions, if we want the half-life, it is better to write the natural logarithm as follows:

$$\ln\frac{[A]_f}{[A]_i} = -k\Delta t$$

And substituting in $\frac{1}{2}[A]_i$ for $[A]_f$, and $t_{\frac{1}{2}}$ for Δt, we get the following:

$$\frac{\left(\ln\frac{1}{2}\right)}{-k} = t_{\frac{1}{2}} \approx \frac{0.693}{k}$$

This is special for first order reaction, because the half-life is a constant for only first order reactions. Therefore, for a first order reaction, the half-life is also concentration independent. Since radioactive decay often follows first order kinetics, we can use the half-life to estimate how much of a radioactive substance is left after a certain period of time.

Chapter 8: Kinetics and Equilibrium

Origins of the Term "Decay"

      If we raise the natural Euler's number e to the power of both sides, we get the following, which explains the word "decay."

$$e^{\ln[A]_f} = e^{\ln[A]_i}e^{-k\Delta t}$$

Since the natural logarithm and the natural exponent do the opposite of each other and cancel out, we now have:

$$[A]_f = [A]_i e^{-k\Delta t}$$

Thus, as the exponent $-k\Delta t$ is negative, using the law of exponents we can do the following:

$$[A]_f = \frac{[A]_i}{e^{k\Delta t}}$$

Which shows that the amount of reactant present is exponentially decaying.

Plotting Another Line

      Just like in the previous case of the zeroth order reaction, our integrated rate law is in the form of a line.

$$\ln[A]_f = \ln[A]_i - k\Delta t$$

$$y = b - mx$$

Thus, for first order reactions, the graph of $\ln[A]$ versus time is linear, with a slope of $-k$, a y-intercept of $\ln[A]_i$, and an x-intercept of $t = \frac{\ln[A]_i}{k}$. However, note that the reaction does not ever stop, as the graph of the exponential decay never reaches zero. When the graph of the integrated rate law hits the x-intercept, the natural logarithm $\ln[A]_f = 0$ simply means that $[A]_f = 1$. Thus, as the line eventually approaches negative infinity, the concentration of A simply approaches zero.

Chapter 8: Kinetics and Equilibrium
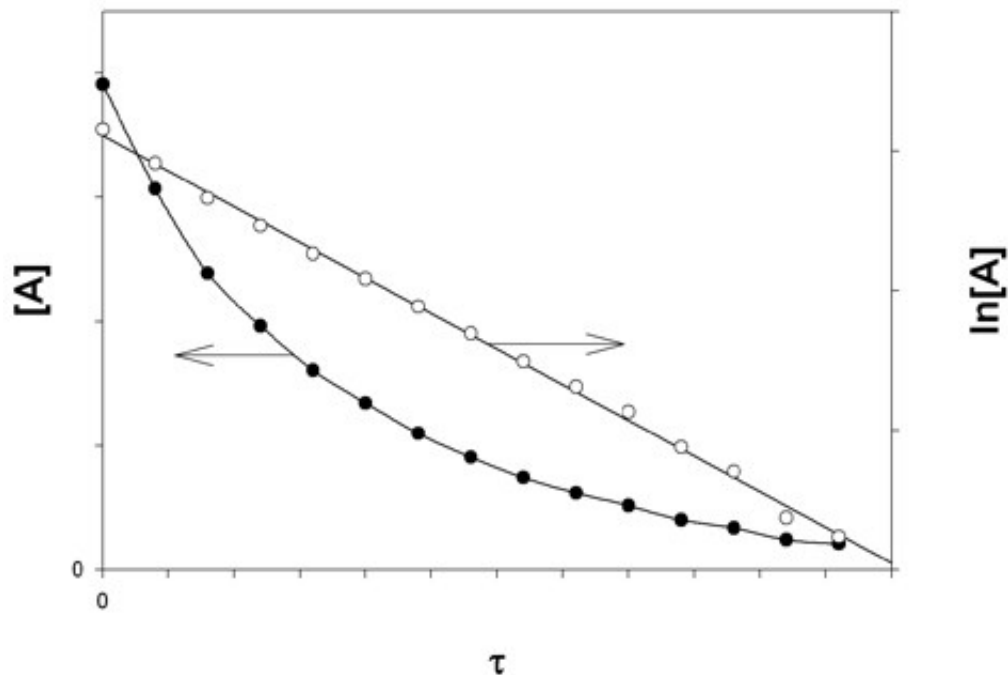
Figure 8.6. For a first order reaction, the plot of concentration versus time is a curve that approaches zero, as shown by the dark circles. Note that the reaction never goes to completion, because there will always be some reactant that did not yet react, as shown by the curve. The graph of the natural logarithm of concentration versus time, as shown by the white circles, is a line. For a first order reaction, after 1 half-life ½ remains, after 2 half-lives 1/4th remains, after three half-lives 1/8th remains, after four half-lives 1/16th remains, and so forth.

Second Order Reactions

For a reaction that is second order with respect to A, we have the following differential rate law:

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^2$$

Thus, we move the $[A]^2$ to the other side, and sum.

$$\frac{d[A]}{[A]^2} = -k dt$$

For summing equations of the form $\frac{d[A]}{[A]^2}$, we have the following rule, which is from the power rule for integration: $\int_i^f \frac{d[A]}{[A]^2} = -\Delta \frac{1}{[A]}$. Thus, we have:

Chapter 8: Kinetics and Equilibrium

$$\int_i^f \frac{d[A]}{[A]^2} = -\frac{1}{[A]_f} - \left(-\frac{1}{[A]_i}\right) = \frac{1}{[A]_i} - \frac{1}{[A]_f} = \int_i^f -kdt = -k\Delta t$$

Therefore, we result in the following:

$$\frac{1}{[A]_f} = \frac{1}{[A]_i} + k\Delta t$$

Now, to find the final concentration of A at time t, we rearrange to get the following:

$$[A]_f = \frac{1}{\dfrac{1}{[A]_i} + k\Delta t} = \frac{[A]_i}{1 + [A]_i k\Delta t}$$

Half-Life

For half-life of the second order reaction, we have:

$$[A]_f = \frac{1}{2}[A]_i$$

$$\frac{2}{[A]_i} - \frac{1}{[A]_i} = kt_{\frac{1}{2}}$$

$$\frac{1}{[A]_i k} = t_{\frac{1}{2}}$$

We find that the half-life for a second order reaction is not as useful as the constant half-life of the first order reaction, because it is concentration dependent and varies throughout the course of the experiment.

Plotting Yet Another Line

Again, for the second order reaction, we notice that our integrated rate law is in the form of a line. Note that this line has a positive slope, whereas the graph of the line for a zeroth and first order integrated rate law leads to a negative slope.

$$\frac{1}{[A]_f} = \frac{1}{[A]_i} + k\Delta t$$

Chapter 8: Kinetics and Equilibrium

$$y = b + mx$$

Here, the y-intercept is equal to $\frac{1}{[A]_i}$, the slope is equal to k, and there is no x intercept, because that would require negative time! Note that again, the reaction never goes to completion, like the first order reaction.
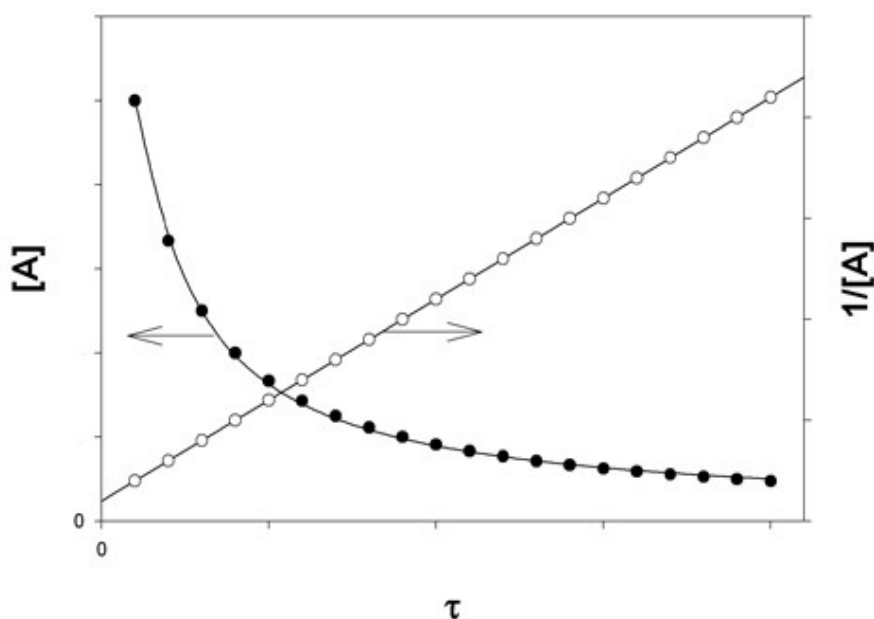
Figure 8.7. The graph of concentration versus time for a second order reaction is also a curve. Notice how here the reaction does not go to completion either, as indicated by the black circles. The graph of 1 over the concentration versus time is a line, as shown by the white circles. The half-life is not very meaningful for second order reactions.

Working with Chemical Equations

Very often, it is useful to use a series of reactions to find a variety of values. When reactions occur after one another, we generally add them. The cancellation of certain species represents the consumption of the species generated in the previous reaction by another reaction. A common example is the reaction of dinitrogen oxide and oxygen to form dinitrogen tetroxide. Let us use this example, which is a reaction at a temperature at SATP (298.15 K, and 1 atm):

$$2N_2O(g) + 3O_2(g) \rightleftharpoons 2N_2O_4(g)$$
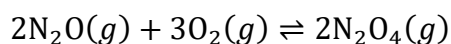
$$\Delta G° = -12.646\,\frac{kJ}{mol}, \Delta H° = -145.780\,\frac{kJ}{mol}, \Delta S° = -446.53\,\frac{J}{mol\ K}$$

Chapter 8: Kinetics and Equilibrium

Note that some of the thermodynamic values are in units of kilojoules, whereas others are in joules. Thus, if we are to work with the values, we should first convert them into joules.

$$\Delta G° = -12646\frac{J}{mol}, \Delta H° = -145780\frac{J}{mol}, \Delta S° = -446.53\frac{J}{mol\ K}$$

$$K_{c,Rxn} = \frac{[N_2O_4]^2}{[N_2O]^2[O_2]^3} = 1.64 * 10^2$$

The Equation Can Be Represented as the Sum of Multiples of the Following Three Equations:

Rxn₁:

$$2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g)$$
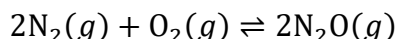
$$\Delta G° = 208422\frac{J}{mol}, \Delta H° = 164100\frac{J}{mol}, \Delta S° = -148.66\frac{J}{mol\ K}$$

$$K_{Rxn_1} = \frac{[N_2O]^2}{[N_2]^2[O_2]} = 3.05 * 10^{-37}$$

Rxn₂:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
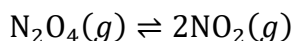
$$\Delta G° = 4776\frac{J}{mol}, \Delta H° = 57200\frac{J}{mol}, \Delta S° = 175.83\frac{J}{mol\ K}$$

$$K_{Rxn_2} = \frac{[NO_2]^2}{[N_2O_4]} = 1.46 * 10^{-1}$$

Rxn₃:

$$Rxn_3 = \frac{1}{2}N_2(g) + O_2(g) \rightleftharpoons NO_2(g)$$
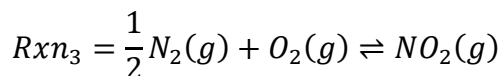
$$\Delta G° = 51332\frac{J}{mol}, \Delta H° = 33180\frac{J}{mol}, \Delta S° = -60.88\frac{J}{mol\ K}$$

$$K_{Rxn_3} = \frac{[NO_2]}{[N_2]^{\frac{1}{2}}[O_2]} = \frac{[NO_2]}{\sqrt{[N_2]}[O_2]} = 1.02 * 10^{-9}$$

Chapter 8: Kinetics and Equilibrium

Thus, to get the equation that we want, we add the balanced equations of the single step reactions, or multiples of the balanced equations of the single step reactions. Here is where we want to apply dimensional analysis. We are putting the equations in series, so that the reactants $2N_2O(g) + 3O_2(g)$, are converted into the product $2N_2O_4(g)$. We see that we can also calculate the change in Gibbs free energy, entropy, and the enthalpy of reaction by multiplying the standard Gibbs free energy and the enthalpy by the same constants. The same can be done with other thermodynamic values, but we will not need them here. Note that when we multiply by moles, the change in enthalpy and Gibbs free energy are now expressed in joules, and the entropy is now expressed in joules per Kelvin, because the moles cancel out.

Calculations for Rxn₁:

$$-1\text{mol}(\text{Rxn}_1) = -2N_2(g) - O_2(g) \rightleftharpoons -2N_2O(g)$$
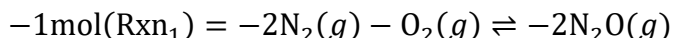
Again, we apply the fact that we can add equivalent quantities to both sides of an equation to arrive at another equation. Here, we add $2N_2(g) + O_2(g) + 2N_2O(g)$ to both sides

$$-2N_2(g) - O_2(g) + [2N_2(g) + O_2(g) + 2N_2O(g)]$$
$$\rightleftharpoons -2N_2O(g) + [2N_2(g) + O_2(g) + 2N_2O(g)]$$
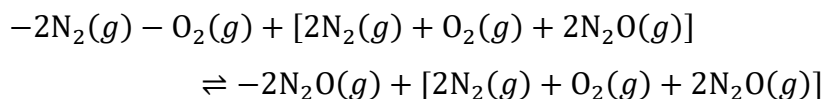
Which, when we combine the terms, we arrive at:

$$2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g)$$
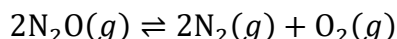
which is just the reverse of the original chemical equation. Thus, we observe that multiplying a chemical equation by a negative simply reverses the equation, and then scales the equation. Here, because we multiplied by negative 1, we reverse the equation, but the scale remains at 1. We will observe scaling when we deal with Rxn₂ and Rxn₃.

Now, note how the equilibrium constant changes in response. This logically follows from the idea of swapping the numerator and denominator of the expression for the equilibrium constant, because we switch the reactants and the products of the forward reaction in order to achieve the reverse reaction. Multiplying an equation by negative 1 essentially reverses the reaction. Therefore, the products and the reactants are now switched. We have the following expression for our equilibrium constant:

Chapter 8: Kinetics and Equilibrium

$$K'_{Rxn_1} = K^{-1}_{Rxn_1} = K_{-1mol(Rxn_1)} = \cfrac{1}{\left(\cfrac{[N_2O]^2}{[N_2]^2[O_2]}\right)} = \cfrac{[N_2]^2[O_2]}{[N_2O]^2} = \cfrac{1}{3.05*10^{-37}}$$

$$= (3.05*10^{-37})^{-1} = 3.28*10^{36}$$

The $'$ or $^{-1}$ means the reverse reaction of K_{Rxn1}. Thus, more generally, if we have K_f for the forward reaction, and $K_r=K' = K^{-1}$ for the reverse reaction, we have:

$$K_r = K' = \frac{1}{K_f} = K_f^{-1}$$

Also note, that by multiplying a balanced reaction by a scaling factor, the thermodynamic quantities are likewise scaled. This is necessary to conserve matter, because the amount of energy exchanged needs to be proportional to the amount of reactants. Thus, twice the amount of reactants means twice the amount of thermodynamic change, three times the amount of reactants means three times the amount of thermodynamic change, and so forth. Note how when we reverse the reaction, what we get is simply the thermodynamic quantity times negative 1. Thus, multiplying the chemical equation by -1 means the reverse reaction, which has the reverse effect of the original reaction. Therefore, it is expected for the change in Gibbs free energy, the change in enthalpy, and the change in entropy to all be multiplied by -1.

$$\Delta G^{\circ}_{-1mol(Rxn_1)} = (-1\text{mol})(208422)\frac{J}{\text{mol}}, \Delta H^{\circ}_{-1mol(Rxn_1)} = (-1\text{mol})(164100)\frac{J}{\text{mol}},$$

$$\Delta S^{\circ}_{-1mol(Rxn_1)} = (-1\text{mol})(-148.66)\frac{J}{\text{mol K}}$$

$$\Delta G^{\circ} = -208422 \text{ J}, \Delta H^{\circ} = -164100 \text{ J}, \Delta S^{\circ} = 148.66\frac{J}{K}$$

Calculations for Rxn₂:

$$-2\text{mol}(Rxn_2) = 4NO_2(g) \rightleftharpoons 2N_2O_4(g)$$

Note that we cut out the unnecessary steps that we took when dealing with Rxn₁, which were necessary to explain why in this case we can simply reverse the original reaction and scale it by a factor of 2. Likewise, all of the thermodynamic values are multiplied by -2 as follows:

Chapter 8: Kinetics and Equilibrium

$$\Delta G^{\circ}_{-2mol(Rxn_2)} = (-2\text{mol})(4776)\frac{J}{\text{mol}}, \Delta H^{\circ}_{-2mol(Rxn_2)} = (-2\text{mol})(57200)\frac{J}{\text{mol}},$$

$$\Delta S^{\circ}_{2mol(Rxn_3)} = (-2\text{mol})(175.83)\frac{J}{\text{mol K}}$$

$$\Delta G^{\circ} = -9553 \text{ J}, \Delta H^{\circ} = -114400 \text{ J}, \Delta S^{\circ} = -351.66\frac{J}{K}$$

Here, because of the reversal and scaling of the chemical equation, the equilibrium constant responds likewise:

$$K_{-2mol(Rxn_2)} = \left(\frac{1}{K_{Rxn_2}}\right)^2 = \left\{\frac{1}{\left(\frac{[NO_2]^2}{[N_2O_4]}\right)}\right\}^2 = \frac{[N_2O_4]^2}{[NO_2]^4} = \left(K'_{Rxn_2}\right)^2 = \left(\frac{1}{1.46*10^{-1}}\right)^2$$

$$= \left(K_{Rxn_2}\right)^{-2} = (1.46*10^{-1})^{-2} = 4.72*10$$

Thus, we see that multiplying a reaction by a scaling factor leads to the equilibrium constant being raised to the power of the scaling factor.

$$K_{Scaling\ factor*Rxn} = (K_{Rxn})^{scaling\ factor}$$

Applying this to the case of multiplying the reaction by -1, we get the same result that we had for Rxn₁:

$$K'_{Rxn} = (K_{Rxn})^{-1}$$

Calculations for Rxn₃:
　　Now, we apply everything we seen before on Rxn₃.

Scaling a reaction by a number just means multiplying all of the coefficients by the number:

$$4\text{mol}(Rxn_3) = 4\left(\frac{1}{2}\right)N_2(g) + 4(1)O_2(g) \rightleftharpoons 4(1)NO_2(g) = 2N_2(g) + 4O_2(g) \rightleftharpoons 4NO_2(g)$$
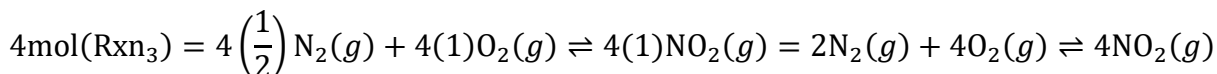
If the scale is negative, we can simply just perform the same addition as we did when dealing with Rxn₁, which essentially just moves the negative reactants to the products side, and the negative products to the reactants side, thus reversing the chemical equation.

Chapter 8: Kinetics and Equilibrium

The thermodynamic quantities are likewise scaled:

$$\Delta G^{\circ}_{4mol(Rxn_3)} = (4\text{mol})(51332)\frac{\text{J}}{\text{mol}}, \Delta H^{\circ}_{4mol(Rxn_3)} = (4\text{mol})33180\frac{\text{J}}{\text{mol}},$$

$$\Delta S^{\circ}_{4mol(Rxn_3)} = (4\text{mol})(-60.88)\frac{\text{J}}{\text{mol K}}$$

$$\Delta G^{\circ} = 205329 \text{ J}, \Delta H^{\circ} = 132720 \text{ J}, \Delta S^{\circ} = -243.53\frac{\text{J}}{\text{K}}$$

And the equilibrium constant is powered:

$$K_{(4mol)Rxn_3} = (K_{Rxn_3})^4 = \left(\frac{[NO_2]}{\sqrt{[N_2][O_2]}}\right)^4 = \frac{[NO_2]^4}{[N_2]^2[O_2]^4} = (1.02*10^{-9})^4 = 1.06*10^{-36}$$

Forming the New Equation

Having scaled all of the equations appropriately, we can add them to form a new equation:

$$\text{New Rxn} = -1\text{mol}(Rxn_1) - 2\text{mol}(Rxn_2) + 4\text{mol}(Rxn_3)$$

New Equation:

$$(-1\text{mol})\text{Reactants}_{Rxn_1} + (-2\text{mol})\text{Reactants}_{Rxn_2} + (4\text{mol})\text{Reactants}_{Rxn_3}$$

$$\rightleftharpoons (-1\text{mol})\text{Products}_{Rxn_1} + (-2\text{mol})\text{Products}_{Rxn_2} + (4\text{mol})\text{Reactants}_{Rxn_3}$$

$$2N_2O(g) + 4NO_2(g) + 2N_2(g) + 4O_2(g) \rightleftharpoons 2N_2(g) + O_2(g) + 2N_2O_4(g) + 4NO_2(g)$$
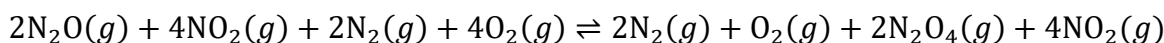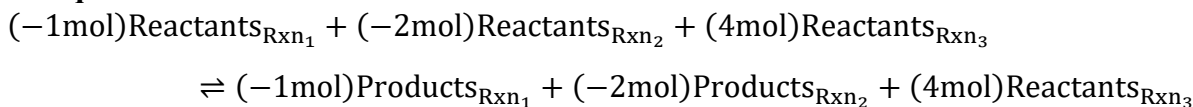
However, we find that there are some species that appear on both sides of the equation. This is because in one reaction, the species are formed, whereas in another reaction, the species are consumed. These are known as intermediates.

To obtain the reaction that we desire, we again apply the principle of equality, and subtract out these species from both sides of the equation. Subtracting out $4NO_2(g) + 2N_2(g) + O_2(g)$ from both sides of the new reaction, we get:

$$2N_2O(g) + 4NO_2(g) + 2N_2(g) + 4O_2(g) - [4NO_2(g) + 2N_2(g) + O_2(g)]$$

$$\rightleftharpoons 2N_2(g) + O_2(g) + 2N_2O_4(g) + 4NO_2(g) - [4NO_2(g) + 2N_2(g) + O_2(g)]$$

Chapter 8: Kinetics and Equilibrium

Desired Equation: $2N_2O(g) + 3O_2(g) \rightleftharpoons 2N_2O_4(g)$
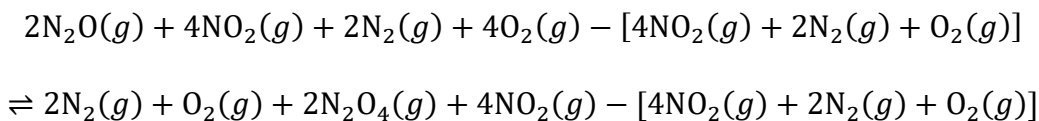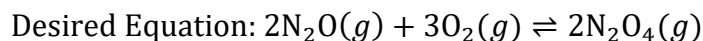
In many common textbooks, this idea of eliminating the intermediates is represented as follows:

$$-1(\text{Rxn}_1) = 2N_2O(g) \rightleftharpoons \cancel{2N_2(g)} + \boldsymbol{O_2(g)}$$

$$-2(\text{Rxn}_2) = \cancel{4NO_2(g)} \rightleftharpoons 2N_2O_4(g)$$

$$4(\text{Rxn}_3) = \cancel{2N_2(g)} + \boldsymbol{4O_2(g)} \rightleftharpoons \cancel{4NO_2(g)}$$
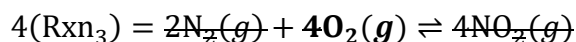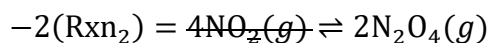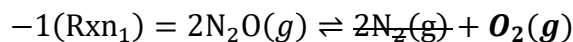
However, the idea is identical, and we arrive at the same answer.

New Thermodynamic Values:

For the change in thermodynamic values, we obtain:

$$\Delta G_{Rxn}^\circ = (-1\text{mol})\left(\Delta G_{Rxn_1}^\circ\right) + (-2\text{mol})\left(\Delta G_{Rxn_2}^\circ\right) + (4\text{mol})\left(\Delta G_{Rxn_3}^\circ\right)$$

$$= (-1\text{mol})(208422)\frac{J}{\text{mol}} + (-2\text{mol})(4776)\frac{J}{\text{mol}} + (4\text{mol})(51332)\frac{J}{\text{mol}}$$

$$= -12646\,J$$

$$\Delta H_{Rxn}^\circ = (-1\text{mol})\left(\Delta H_{Rxn_1}^\circ\right) + (-2\text{mol})\left(\Delta H_{Rxn_2}^\circ\right) + (4\text{mol})\left(\Delta H_{Rxn_3}^\circ\right)$$

$$= (-1\text{mol})(164100)\frac{J}{\text{mol}} + (-2\text{mol})(57200)\frac{J}{\text{mol}} + (4\text{mol})(33180)\frac{J}{\text{mol}}$$

$$= -145780\,J$$

$$\Delta S_{Rxn}^\circ = (-1\text{mol})\left(\Delta S_{Rxn_1}^\circ\right) + (-2\text{mol})\left(\Delta S_{Rxn_2}^\circ\right) + (4\text{mol})\left(\Delta S_{Rxn_3}^\circ\right)$$

$$= (-1\text{mol})(-148.66)\frac{J}{\text{mol K}} + (-2\text{mol})(175.83)\frac{J}{\text{mol K}}$$

$$+ (4\text{mol})(-60.88)\frac{J}{\text{mol K}} = -446.53\frac{J}{K}$$

Note here that we round, because the original values were rounded, and very precise answers were not expected due to rounding error.

Chapter 8: Kinetics and Equilibrium

Checking with a Thermodynamics Relation, and Hess's Law

To check our answer, we can apply the relation that we had from chapter 5, for the change in standard Gibbs free energy:

$$\Delta G° = \Delta H° - T(\Delta S°)$$

Plugging in -145780 J for $\Delta H°$, $-446.53 \frac{J}{K}$ for $\Delta S°$, and 298.15 K for T, we indeed obtain approximately the correct value for $\Delta G°$. However, note that because of rounding, there is some error. We use significant figures to keep track of the precision of our results. We find that the last significant figure is in the ones place, and we observe that the first digit with a discrepancy is in the units.

When we added the thermodynamic changes associated with each of the individual reactions to obtain the thermodynamic changes associated with the equation of interest, we implicitly applied the first law of thermodynamics, that energy was conserved. This result of the conservation of energy is known as Hess's law of constant heat summation, which was published in Germain Henri Hess's 1840 paper "Recherches Thermochimiques." Hess's law is based upon the fact that the energy of the universe is a constant, and that enthalpy is a state function that only depends on the current circumstances of the system of interest. This allows for us to find the thermodynamic change associated with reactions that may not even be possible. Thus, many times, when calculating whether or not a reaction is spontaneous by applying the Gibbs free energy equation, the enthalpy may be based off of calculations using results of other reactions that sum to the reaction of interest, because the reaction of interest may not even occur.

New Equilibrium Constant:

For the final reaction, we can find the equilibrium constant, because we know the equilibrium constant of the individual reactions. Here is where some dimensional analysis is helpful. Looking at the final chemical equation that we had, we can write its equilibrium constant as follows:

$$2N_2O(g) + 3O_2(g) \rightleftharpoons 2N_2O_4(g)$$

Chapter 8: Kinetics and Equilibrium
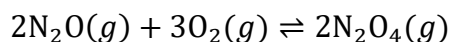
$$\text{Equilibrium Constant} = K_{Rxn} = \frac{[N_2O_4]^2}{[N_2O]^2[O_2]^3} = 1.64 * 10^2$$

To assist us in the process, let us also look at the equivalent new equation that we got by adding the three scaled reactions together:

$$2N_2O(g) + 4NO_2(g) + 2N_2(g) + 4O_2(g) \rightleftharpoons 2N_2(g) + O_2(g) + 2N_2O_4(g) + 4NO_2(g)$$
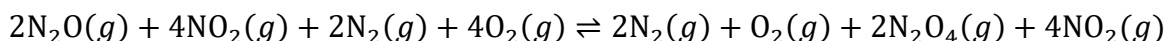
$$\text{Equilibrium Constant} = K_{New\ Rxn} = \frac{[N_2]^2[O_2][N_2O_4]^2[NO_2]^4}{[N_2O]^2[NO_2]^4[N_2]^2[O_2]^4}$$

Since the two equations are equal, and on the same scale, their equilibrium constants should be the same:

$$K_{Rxn} = \frac{[N_2O_4]^2}{[N_2O]^2[O_2]^3} = K_{New\ Rxn} = \frac{[N_2]^2[O_2][N_2O_4]^2[NO_2]^4}{[N_2O]^2[NO_2]^4[N_2]^2[O_2]^4}$$

When we simplify the $K_{New\ Rxn}$, we indeed do get the same thing! We find that when we subtracted out $4NO_2(g) + 2N_2(g) + O_2(g)$ from the reaction to simplify the equation, the corresponding portions of the equilibrium constant were divided out. However, the purpose of showing this is revealed by looking at the equilibrium constants of the scaled reactions:

$$K_{(-1mol)(Rxn_1)} = \left(K_{Rxn_1}\right)^{-1} = \frac{[N_2]^2[O_2]}{[N_2O]^2} = 3.28 * 10^{36}$$

$$K_{(-2mol)(Rxn_2)} = \left(K_{Rxn_2}\right)^{-2} = \frac{[N_2O_4]^2}{[NO_2]^4} = 4.72 * 10$$

$$K_{(4mol)(Rxn_3)} = \left(K_{Rxn_3}\right)^{4} = \frac{[NO_2]^4}{[N_2]^2[O_2]^4} = 1.06 * 10^{-36}$$

We notice that $K_{New\ Rxn} = \frac{[N_2]^2[O_2][N_2O_4]^2[NO_2]^4}{[N_2O]^2[NO_2]^4[N_2]^2[O_2]^4}$ which is equal to $K_{Rxn} = \frac{[N_2O_4]^2}{[N_2O]^2[O_2]^3}$ can be obtained by multiplying the equilibrium constants of the scaled reactions together!

$$K_{New\ Rxn} = K_{(-1mol)(Rxn_1)} * K_{(-2mol)(Rxn_2)} * K_{(4mol)(Rxn_3)}$$

$$\frac{[N_2]^2[O_2][N_2O_4]^2[NO_2]^4}{[N_2O]^2[NO_2]^4[N_2]^2[O_2]^4} = \frac{[N_2]^2[O_2]}{[N_2O]^2} * \frac{[N_2O_4]^2}{[NO_2]^4} * \frac{[NO_2]^4}{[N_2]^2[O_2]^4}$$

Chapter 8: Kinetics and Equilibrium

Therefore, because $K_{New\,Rxn}$ is equal to the product of the equilibrium constants of the scaled equations that make up the reaction, and $K_{New\,Rxn}$ is equal to K_{Rxn}, we find that the equilibrium constant of a desired equation can be found by multiplying the equilibrium constants of equations that add up to yield the desired equation.

Checking with Another Thermodynamic Relation

Another equation that is frequently useful, is the following, which we will use to check our result.

$$\Delta G^\circ = -RT \ln K$$

This equation allows for us to find the standard change in Gibbs free energy for a reaction, given its equilibrium constant, and the temperature at which the reaction proceeds. Substituting in the value of K that we obtained, $1.64 * 10^2$, and 298.15 K for T, we get approximately the same value of ΔG° that we obtained before. Note that because of a property of the logarithm, $n \ln K = \ln K^n$, and scaling the reaction by multiplication leads to corresponding multiplication of the change in Gibbs free energy, but raises the equilibrium constant to the power that we are multiplying by. This is consistent with what we have observed before. Applying this equation to the above, we find that this equation agrees with our calculations. Also, note that the natural logarithm of 1 is equal to zero. Thus, we find that for reactions that are thermodynamically favorable, the equilibrium constant is greater than 1, thus making the change in Gibbs free energy of the reaction negative. Likewise, for reactions that are thermodynamically unfavorable, the change in Gibbs free energy is positive, and the equilibrium constant is less than one. Thus, we find that equilibrium is a thermodynamic property of the system, and for a spontaneous reaction, where $\Delta G < 0$ and $K > 1$, the reverse reaction is nonspontaneous, and $\Delta G_{reverse} > 0$, and $K < 1$, and vice versa.

Equilibrium Constants and Thermodynamic Quantities for a Series of Reactions

For the Following Generic Series of Reactions:
$$Rxn = Rxn_1 + Rxn_2 + Rxn_3 + \cdots$$

Chapter 8: Kinetics and Equilibrium

Which is the Same as:
$$\text{Rxn} = \text{Reactants}_{\text{Rxn}_1} + \text{Reactants}_{\text{Rxn}_2} + \text{Reactants}_{\text{Rxn}_3} + \cdots$$
$$\rightleftharpoons \text{Products}_{\text{Rxn}_1} + \text{Products}_{\text{Rxn}_2} + \text{Products}_{\text{Rxn}_3} + \cdots$$
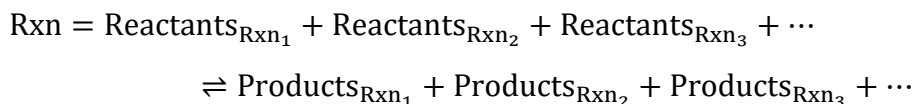
The Series of Reactions Will Have an Equilibrium Constant Equal To:
$$K_{Rxn} = K_{Rxn_1} * K_{Rxn_2} * K_{Rxn_3} * \ldots$$

And the Series of Reactions Will Have Thermodynamic Values That Are Equal To:
$$\Delta H^{\circ}_{Rxn} = \Delta H^{\circ}_{Rxn_1} + \Delta H^{\circ}_{Rxn_2} + \Delta H^{\circ}_{Rxn_3} + \cdots$$

$$\Delta G^{\circ}_{Rxn} = \Delta G^{\circ}_{Rxn_1} + \Delta G^{\circ}_{Rxn_2} + \Delta G^{\circ}_{Rxn_3} + \cdots$$

And so forth for all the thermodynamic state functions.

Kinetics for Multistep Reactions

The Rate-Determining Step

When there is a multi-step reaction where all the individual steps of the overall multi-step reaction are occurring at once, the rate of the overall reaction is equal to the rate of the slowest reaction. The slowest reaction is known as the rate determining step, or the slow step. This is because the reaction cannot proceed any faster than the slowest step of the process. Let's say that there is a traffic jam. The roads leading up to the intersection are very wide. However, during each green light, only 20 cars can go. Then the light turns red again.

Chapter 8: Kinetics and Equilibrium

Figure 8.8. A busy intersection. No matter how fast cars arrive at the intersection, the rate of the number of cars that can pass is limited to a fixed rate by the intersection.

In this situation, no matter how many cars arrive at the intersection, the rate is set at 20 cars per green light. The rate of movement of vehicles at that intersection is set by the slowest step. Likewise, the rate of the multi-step reaction cannot exceed the rate of the slowest reaction. Thus, the determination of rate for a reaction can reveal important details about the mechanism of a reaction.

An Example of Multistep Reaction Kinetics

$$4HBr(g) + O_2(g) \rightarrow 2H_2O(g) + 2Br_2(g)$$
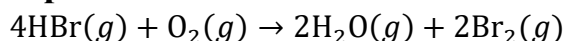
If we experimentally determine that the reaction proceeds according to the elementary steps

$$\text{Step 1: } HBr(g) + O_2(g) \rightleftharpoons HO_2Br(g)$$
$$\text{Step 2: } HO_2Br(g) + HBr(g) \rightleftharpoons 2HOBr(g)$$
$$\text{Step 3: } HOBr(g) + HBr(g) \rightleftharpoons H_2O + Br_2(g)$$
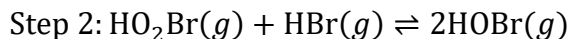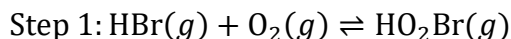
We find that step 1 followed by step 2 followed by two times step 3 gives us the overall equation.

If the reaction's rate is equal to

Chapter 8: Kinetics and Equilibrium

$$\text{Rate} = k_{1f}[\text{HBr}][\text{O}_2]$$

Then, we know that the first step is the slow step. However, if the second step is the slow step, we need to do a little bit of math to figure out what is the form of the rate law that we expect. Note how all of the arrows are equilibrium arrows. That is because, in most reactions, the individual elementary step reactions are reversible to some extent. So, to get the rate law of the second step, we do the following:

$$\text{Rate}_2 = k_{2f}[\text{HO}_2\text{Br}][\text{HBr}]$$

where k_{2f} is the forward rate constant for reaction two, and we solve for the concentration of HO_2Br, which we need because it is not given as an initial reactant, and is rather formed as an intermediate.

The Steady State Approximation

Thus, to solve for the missing intermediate species, we approximate. We do something called the steady-state approximation, which basically means that we assume that all of the steps before the slow step reaches equilibrium as the reaction proceeds, because the slow step is so slow that it allows the reactions before it to form a steady amount of intermediate. Now, since the forward and reverse rates are equal when the reaction is at equilibrium, we do the following:

$$\text{Rate}_{1f} = \text{Rate}_{1r}$$

$$k_{1f}[\text{HBr}][\text{O}_2] = k_{1r}[\text{HO}_2\text{Br}]$$

And solving for $[\text{HO}_2\text{Br}]$, we get:

$$\frac{k_{1f}[\text{HBr}][\text{O}_2]}{k_{1r}} = [\text{HO}_2\text{Br}]$$

With the concentration of the intermediate expressed in terms of only reactants given and rate constants, we substitute back into the rate expression for reaction 2. Thus, we have:

$$\text{Rate}_2 = k_{2f}[\text{HO}_2\text{Br}][\text{HBr}] = \frac{k_{2f}k_{1f}}{k_{1r}}[\text{HBr}][\text{O}_2][\text{HBr}]$$

Chapter 8: Kinetics and Equilibrium

We can express the previous with a new rate constant, or even just replace $\frac{k_{1f}}{k_{1r}}$ with K_1, or the equilibrium constant of the single step reaction 1.

$$\text{Rate} = k_{new}[\text{HBr}]^2[\text{O}_2], \text{where } k_{new} = \frac{k_{2f}k_{1f}}{k_{1r}}$$

$$\text{Rate} = k_{2f}K_1[\text{HBr}]^2[\text{O}_2]$$

And, if the third reaction is the slow step, we do the same process again, except just using the rate expression of the third reaction, and performing the steady state approximation on reactions 1 and 2. However, do note, that if the experimental reaction rate law is $\text{Rate} = k[\text{HBr}][\text{O}_2]$, then we know that the slow step is reaction 1, and if the experimental reaction rate law is $\text{Rate} = k[\text{HBr}]^2[\text{O}_2]$, we know that reaction 2 is the slow step, and so forth. The slowest step is the rate determining step, as we have discussed before, and to track the progress of a reaction, we only need to track the progress of the rate determining step, because the earlier reactions are in quick equilibrium, and the later reactions consume the products of the rate determining step nearly instantaneously to finish the reaction.

Equations Relating Kinetic, Equilibrium, and Thermodynamic Properties, from the Perspective of Le Chatelier's Principle

Le Chatelier's Principle

Le Chatelier's principle is an empirical rule set forth by Henry Louis Le Chatelier in 1884, and independently discovered by Karl Ferdinand Braun. It states that a system at equilibrium, if disturbed, will try to restore equilibrium. Thus, if any action is done to the system, the reaction will shift in a way to counteract that action.

For example, if the reaction allows for change in the number of moles of gas, increasing pressure by decreasing volume of the container would drive the reaction in the direction where the number of moles of gas is minimized. If some new substance is added, the reaction will proceed to lessen the amount of that type of gas. If a catalyst is added, nothing happens, as the catalyst does not actively participate as a reactant nor a product, and speeds up reactions in both directions, thus leading to no effect.

Chapter 8: Kinetics and Equilibrium

However, changing the temperature changes the equilibrium constant. That is because the temperature is a thermodynamic quantity, and the equilibrium constant is an associated thermodynamic quantity that changes with respect to changes in temperature. Thus, if a reaction is exothermic, increasing the temperature of the reaction vessel will decrease the equilibrium constant, in order to decrease the amount of heat generated by the reaction. If the reaction is endothermic, then the opposite will occur.

Le Chatelier's principle is a good rule of thumb for predicting the direction that the system will proceed when disturbed, but does not tell us the extent to which the system will respond. Thus, other thermodynamic information needs to be provided for us to be able to calculate anything, and the principle is only good as a rule of thumb that nearly always works (unless if the reaction cannot proceed). The Initial, Change, and Equilibrium (ICE) table is a good way to remember how to calculate equilibrium concentrations and pressures. However, it is good to keep in mind that what we are really calculating with the "ICE" table, is the amounts of each reactant and product that the system reacts towards.

Also, note that when we disturb the system, the system will shift to reduce the influence of our disturbance, but will never be able to eliminate the disturbance. Thus, the system cannot equally compensate (completely undo the effects of the disturbance). nor overcompensate (react to create the opposite effect of the disturbance when compared to the initial state of the system). The system can **only** undercompensate, and **lessen the effects of the disturbance!**

The van't Hoff Equation

If we know the equilibrium constant for a reaction at one temperature, we can easily find the equilibrium constant at another temperature, given that the two temperatures are close together, using the following formula, which is the van't Hoff equation:

$$\ln\frac{K_2}{K_1} = \frac{\Delta H°}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

The van't Hoff equation relates the equilibrium constant to temperature, and its derivation is provided. The results of change in temperature is summarized as follows:

Change in Enthalpy	$T_2 > T_1$	$T_2 < T_1$
$\Delta H > 0$	K increases	K decreases
$\Delta H < 0$	K decreases	K increases

According to Le Chatelier's principle, this makes sense. If the reaction releases heat $\Delta H_{rxn}° < 0$, then adding heat to the system will drive the reaction in the opposite direction, causing less of the reaction to occur, thus releasing less heat, and vice versa.

The Clausius Clapeyron Equation

For the special case where there is only one substance in equilibrium with itself, the Clausius-Clapeyron equation is useful. The Clausius-Clapeyron equation is written for vapor pressure, but may also be used for some other purposes as well, because it is very versatile.

$$\ln \frac{P_{vap,T_2}}{P_{vap,T_1}} = \frac{\Delta H_{vap}°}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Since the change in enthalpy of vaporization is nearly always positive, as energy needs to be absorbed for bonds to be broken in order for the substance to evaporate, when the temperature increases, it is expected that the vapor pressure increases as well. This can be demonstrated with some rubbing alcohol, two bottles cold water, hot water, and a lighter. When we put a few drops of alcohol in the two bottles, and put one bottle in hot water, and the other in cold water, and ignite the alcohol vapor, we get a far more larger flame with the bottle that is in hot water. This is because the vapor pressure of alcohol increases as temperature increases, which leads to a greater alcohol vapor concentration for the bottle which is at a higher temperature.
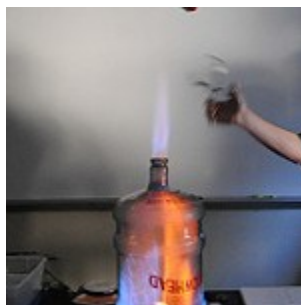
Figure 8.9. The whoosh bottle is a classical classroom demonstration, where rubbing alcohol vapor is ignited.

257

Chapter 8: Kinetics and Equilibrium

The Arrhenius Equation

A third equation, which results from experimental evidence, is the Arrhenius equation, which relates rate constants to temperatures. The Arrhenius equation can be written in exponential, logarithmic, and two-point form.

Arrhenius Equation: $k = Ae^{-\frac{E_a}{RT}}$, where A is a constant, E_a is the activation energy, and R is the molar gas constant

Arrhenius Equation in logarithmic form: $\ln k = -\dfrac{E_a}{RT} + \ln A$,

Arrhenius Equation in "two-point" form: $\ln \dfrac{k_{T_2}}{k_{T_1}} = \dfrac{E_a}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

Since the activation energy is always positive, as a certain amount of energy is required for the reactants to collide hard enough to react, an increase in temperature nearly always leads to an increase in the rate of reaction. Although the activation energy was originally defined by Arrhenius as an energy barrier that prevents reaction, the activation energy is better defined in a modern sense as a free energy barrier that prevents reaction, because energetically unfavorable reactions happen readily if the reaction is sufficiently entropically favorable. Thus, in modern practice, E_a is commonly represented as $\Delta G^{\ddagger}$, which is the free energy required for the reactants to reach the transition state necessary for the reaction to proceed. Note that the change in Gibbs free energy of reaction is a thermodynamic quantity, which affects equilibrium, whereas the transition state Gibbs free energy barrier is a kinetic quantity, which affects rate.

Chapter 8: Kinetics and Equilibrium
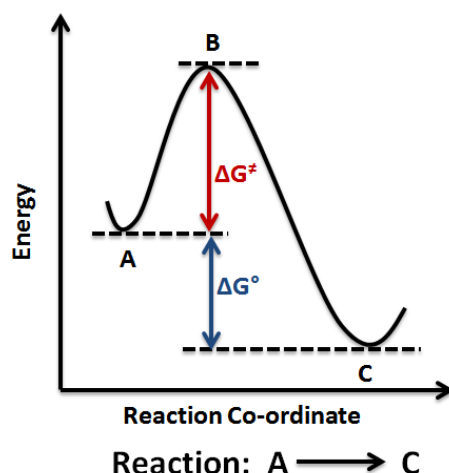
Figure 8.10. The reaction coordinate graph for the reaction that consumes A and creates C. Note that thermodynamic favorability is determined by change in Gibbs free energy, $\Delta G°$, and kinetic favorability is determined by the difference between the initial Gibbs free energy and the transition state kinetic energy, $\Delta G^{\ddagger}$. Equilibrium is governed by the change in Gibbs free energy, and reaction rate is governed by the transition state free energy requirement.

An historically important observation that corresponds well to the Arrhenius equation, is that the rate of most reactions that occur at around room temperature usually roughly doubles for every 10-degrees Celsius increase in temperature. This is expected, because raising the temperature increases the energy of the molecules. The increase in energy leads to an increase in velocity, which increases both the frequency of collision, and the probability that the molecules colliding have enough energy to react.

Applicability of Le Chatelier's Principle

Le Chatelier's principle, although based off empirical observations, can be kept in mind whenever there is an equilibrium. It is almost always relevant, and allows for a quick determination of the direction of reaction. However, we need to be careful in the case that there is no reaction at all. A system containing a mixture of sand and sawdust will not react to counteract the effects of increasing the volume of the container that the mixture is in. In those cases, the principle is irrelevant, because there is no change that occurs. In terms of usefulness, it has diverse applications in many practices, including economics. In short, the all the principle means, is that a stable system will seek to reduce the impact of a disturbing event. Thus, if we do

Chapter 8: Kinetics and Equilibrium

something to a system to disturb its equilibrium, the system will try to do the opposite of what we did. However, do keep in mind that equilibrium is a thermodynamic quantity, and if the reaction does not occur, there is simply no equilibrium because there is no thermodynamic change.

Equilibrium Constant Does Not Change, unless if Temperature Changes

Keep in mind that the equilibrium constant does not change, except when the temperature changes, because equilibrium is a thermodynamic property. The equilibrium constant obviously does not change when some substance that does not participate in the reaction is added to the reaction vessel. Also, the equilibrium constant will not change when the amount of pure solid in the system is changed, because the concentration of the pure solid is roughly constant. Thus, as long as the pure solid exists, and is not completely consumed, the equilibrium holds. Although the rate may change with the addition of a catalyst, the equilibrium is undisturbed, because the catalyst speeds up the reaction in both directions by lowering the transition state Gibbs free energy requirement $\Delta G^{\ddagger}$, and essentially multiplies the forward and reverse rate constants by a factor.

$$k_{catalyzed\,f} = k_{uncatalyzed\,f} * g_1$$

$$k_{catalyzed\,r} = k_{uncatalyzed\,r} * g_2$$

Where g_1 and g_2 is some constant, and g_1 is equal to g_2. Thus, they cancel when they are divided

$$K = \frac{k_f}{k_r} = \frac{k_{uncatalyzed\,f}}{k_{uncatalyzed\,r}} = \frac{k_{uncatalyzed\,f} * g_1}{k_{uncatalyzed\,r} * g_2} = \frac{k_{catalyzed\,f}}{k_{catalyzed\,r}}$$

This also makes sense, because if the catalyst is regenerated, the thermodynamic change associated with the reaction is the same as if the catalyst is not present, thus the equilibrium constant, which is also a thermodynamic quantity, is unchanged by the presence of the catalyst. Therefore, we find that the catalyst has no effect on equilibrium, unless if the reaction does not occur without the catalyst.

Chapter 8: Kinetics and Equilibrium

Chapter 9: Kinetics and Equilibrium Derivations

We begin with our fundamental relation, which we derived previously, in order to find some relations that we need.

$$dG = V dp - S dT$$

We apply an isothermal restriction, because Gibbs free energy is primarily useful when temperature is held constant.

$$dG = V dp$$

We use the ideal gas law, to approximate the volume.

$$pV = nRT$$

$$V = \frac{nRT}{p}$$

$$dG = \frac{nRT}{p} dp$$

Integrating, we get:

$$\int_i^f dG = \int_i^f \frac{nRT}{p} dp$$

And, when temperature and number of moles are kept constant, we get the following:

$$\Delta G = G_f - G_i = nRT \ln\left(\frac{p_f}{p_i}\right),$$

where f and i are the final and initial states, and T, n are kept constant.

We Standardize:

If we standardize the reaction, where $p_i = 1 \text{ atm} = P°$, we get the following, where G is the Gibbs free energy of the current state of the ideal gas.

$$G - G° = nRT \ln(P), \text{where } P \text{ is in atm, and } n, T \text{ are kept constant}$$

We can find the change in Gibbs free energy of a reaction using this formula by finding the Gibbs free energy of the products, and subtracting the Gibbs free energy of the reactants. Note that here, because we are working with thermodynamic quantities, the gas constant is equal to $8.314 \frac{\text{J}}{\text{mol K}}$. Thus, for the generic reaction below, where we use the pressure expression for the equilibrium constant, we have the following:

$$\alpha A + \beta B + \gamma C + \cdots \rightleftharpoons \omega Z + \psi Y + \cdots$$

$$\Delta G_{rxn} = \Sigma \Delta G_{products} - \Sigma \Delta G_{reactants}$$

The following depends on the properties of logarithms, that $k \ln A = \ln A^k$, $\ln A + \ln B = \ln AB$, and $\ln A - \ln B = \ln \frac{A}{B}$. Thus, for every product, we add $G_{product} - G°_{product} = RT\, n_f \ln P_f = RT \ln P_f^{n_f}$, and for every reactant we subtract $G_{reactant} - G°_{reactant} = RT\, n_i \ln P_i = RT \ln P_i^{n_i}$ (note how here the subscripts $_f$ and $_i$ indicate the products and the reactants, and do not stand for final nor initial states of the reactant or product they are attached to, because using the subscript $_p$ for products may be confusing as pressure is also symbolized by P. Thus, the subscripts are best thought of the initial system, before the reaction, and the final system, after the reaction).

$$\left(G_{products} - G_{products}°\right) - \left(G_{reactants} - G_{reactants}°\right)$$

$$= \Delta G_{rxn} - \Delta G_{rxn}° = RT\left(\Sigma\, n_{product} \ln P_{product} - \Sigma\, n_{product} \ln P_{reactant}\right)$$

$$Rxn: \alpha A + \beta B + \gamma C + \cdots \rightleftharpoons \omega Z + \psi Y + \cdots$$
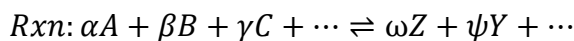
$$\Delta G_{rxn} - \Delta G_{rxn}° = RT \ln \left(\frac{(P_Z)^\omega (P_Y)^\psi * \cdots}{(P_A)^\alpha (P_B)^\beta (P_C)^\gamma * \cdots} \right)$$

Note how the fraction inside of the parentheses look like the equilibrium expression:

$$K_p = \frac{k_{pf}}{k_{pr}} = \frac{(p_Z)^\omega (p_Y)^\psi * \cdots}{(p_A)^\alpha (p_B)^\beta (p_C)^\gamma * \cdots}$$

Chapter 9: Kinetics and Equilibrium Derivations

That expression, $\frac{(P_Z)^\omega (P_Y)^\psi *...}{(P_A)^\alpha (P_B)^\beta (P_C)^\gamma *...}$ is called the reaction quotient, or Q. The relation between the reaction quotient and the equilibrium constant, is that as the reaction goes to equilibrium, the reaction quotient becomes the equilibrium constant. Thus, if the reaction quotient is larger than the equilibrium constant, the reaction reverses, and if the reaction quotient is smaller than the equilibrium constant, the reaction proceeds. Note that the reaction quotient and the Gibbs free energy of the system changes as the reaction proceeds, but the equilibrium constant and the standard change in Gibbs free energy for the reaction are only dependent upon the initial and final states, and are therefore constant for the given reaction, unless if there is a temperature change.

Thus, we can rewrite the equation as follows:
$$\Delta G_{rxn} - \Delta G_{rxn}° = RT \ln Q$$

This expression allows us to find the change in Gibbs free energy of reaction at any temperature using any concentration of reactants, if we know the standard Gibbs free energies of the reactants and products, the reaction quotient expression, and the temperature of the reaction. However, this equation is the most interesting, when the reaction is at equilibrium. At equilibrium, the reaction does not tend towards any direction, and the pressures are stable. Also, at equilibrium, the reaction quotient, Q, is equal to the equilibrium constant, K. This implies that the Gibbs free energies of the products and reactants are equal, and that the change in Gibbs free energy for the reaction in both directions is equal to zero.

$$0 - \Delta G° = RT \ln K \text{ , at equilibrium}$$

Thus, we get a relation between the standard change in Gibbs free energy and the equilibrium constant.

Relation Between Standard Change in Gibbs Free Energy and the Equilibrium Constant
$$\Delta G° = -RT \ln K$$

Chapter 9: Kinetics and Equilibrium Derivations

Note that because of a property of the logarithm, $n \ln K = \ln K^n$, and scaling the reaction by multiplication leads to corresponding multiplication of the change in Gibbs free energy, but raises the equilibrium constant to the power that we are multiplying by.

Derivation of the Integrated Clausius-Clapeyron Equation

Using a result that we had while deriving this equation, $\Delta G - \Delta G° = nRT \ln(P)$, we can derive another equation which relates the vapor pressure of a liquid at two temperatures. When a liquid is at a given temperature, a certain portion of the liquid evaporates. At that temperature, as long as there is some liquid that remains, the pressure of the gas reaches that equilibrium vapor pressure, regardless of the volume of the container or the amount of liquid present. A favorite demonstration of vapor pressure involves putting a small amount of rubbing alcohol in a water bottle, and then proceeding to ignite the isopropyl alcohol vapor. Thus, in this case, the P is the vapor pressure of the same chemical. Note that for equilibrium to occur, as discussed previously, the Gibbs free energy must be zero. Thus, $\Delta G = 0$ when $P = P_{vap} = P_{equlibrium}$.

$$\Delta G - \Delta G° = nRT \ln(P)$$

$$0 - \Delta G° = nRT \ln P_{vap}$$

$$\Delta G° = -nRT \ln P_{vap}$$

It is easier to perform the derivation using the Gibbs free energy for one mole, where $n=1$. Remember that we can always scale the equation later, by multiplying by a constant.

$$\Delta G° = -RT \ln P_{vap}$$

Now, we isolate the $\ln P_{vap}$.

$$\ln P_{vap} = -\frac{\Delta G°}{RT}$$

To get the relation between the vapor pressure at two different temperatures, $P_{vap\ T_1}$ and $P_{vap\ T_2}$, we do the following:

Chapter 9: Kinetics and Equilibrium Derivations

$$\ln P_{vap\,T_1} = -\frac{\Delta G^\circ}{RT_1}$$

$$\ln P_{vap\,T_2} = -\frac{\Delta G^\circ}{RT_2}$$

Now, we subtract the two:

$$\ln P_{vap\,T_2} - \ln P_{vap\,T_1} = \ln\frac{P_{vap\,T_2}}{P_{vap\,T_1}} = -\frac{\Delta G^\circ}{RT_2} + \frac{\Delta G^\circ}{RT_1}$$

Now, we expand out the two standard Gibbs free energies:

$$\ln\frac{P_{vap\,T_2}}{P_{vap\,T_1}} = -\left[\frac{\Delta H_{vap}{}^\circ}{RT_2} - \frac{T_2\Delta S_{vap}{}^\circ}{RT_2}\right] + \left[\frac{\Delta H_{vap}{}^\circ}{RT_1} - \frac{T_1\Delta S_{vap}{}^\circ}{RT_1}\right]$$

$$= \frac{-\Delta H_{vap}{}^\circ}{RT_2} + \frac{\Delta H_{vap}{}^\circ}{RT_1} + \frac{\Delta S_{vap}{}^\circ}{R} - \frac{\Delta S_{vap}{}^\circ}{R}$$

$$\ln\frac{P_{vap\,T_2}}{P_{vap\,T_1}} = -\frac{\Delta H_{vap}{}^\circ}{RT_2} + \frac{\Delta H_{vap}{}^\circ}{RT_1} = \frac{\Delta H_{vap}{}^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Thus, we have our following result, which relates the vapor pressures of a liquid at two different temperatures:

$$\ln\frac{P_{vap\,T_2}}{P_{vap\,T_1}} = \frac{\Delta H_{vap}{}^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

This is known as the "two-point" form of the integrated Clausius-Clapeyron equation, because we can calculate a vapor pressure at another temperature if we know the vapor pressure at another temperature, or a temperature at one vapor pressure if we know the vapor pressure at another temperature, and vice versa.

Common Applications of This Equation, and Other Equations of Similar Form Involves the Following:

$$\text{If } \frac{f(x)}{g(x)} = \text{a constant}$$

Then, plotting $f(x)$ versus $g(x)$ on y and x results in a line.

Chapter 9: Kinetics and Equilibrium Derivations

Thus, we find in our equation, that $\frac{\Delta H_{vap}°}{R}$ is a constant, because the standard change in enthalpy for vaporization is a constant, and the molar gas constant, since we are working with thermodynamic quantities, is equal to $8.314 \frac{J}{mol\ K}$. Thus, rearranging the equation, we find:

$$\frac{\left(\ln \frac{P_{vap\ T_2}}{P_{vap\ T_1}}\right)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} = \frac{\Delta H°}{R} = \text{a constant}$$

Thus, a plot of $\left(\ln \frac{P_{vap\ T_2}}{P_{vap\ T_1}}\right)$ versus $\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ results in a line, which is commonly used as a convenient way to graph the Clausius-Clapeyron equation, and also equations of similar form.

Derivation of the Integrated van't Hoff Equation

Repeating a similar process with

$$\Delta G_{rxn}° = -RT \ln K$$

Yields another useful result, called the integrated van't Hoff equation, named after Jacobus Henricus van't Hoff Junior, who published it in his 1884 book "Studies in Dynamic Chemistry." The van't Hoff equation allows for us to calculate changes in equilibrium constants at different temperatures. So, we begin the derivation:

$$\Delta G_{rxn}° = -RT \ln K$$

Again, we isolate the natural logarithm, $\ln K$.

$$\ln K = -\frac{\Delta G_{rxn}°}{RT}$$

We subtract the equilibrium constants for two different temperatures.

$$\ln K_{T_1} = \frac{-\Delta G_{rxn}°}{RT_1}$$

$$\ln K_{T_2} = \frac{-\Delta G_{rxn}°}{RT_2}$$

Chapter 9: Kinetics and Equilibrium Derivations

$$\ln K_{T_2} - \ln K_{T_1} = \ln \frac{K_{T_2}}{K_{T_1}} = \frac{-\Delta G_{rxn}°}{RT_2} + \frac{\Delta G_{rxn}°}{RT_1}$$

Just like in the previous derivation, we expand out our Gibbs free energies:

$$\ln \frac{K_{T_2}}{K_{T_1}} = -\left[\frac{\Delta H_{rxn}°}{RT_2} - \frac{T_2 \Delta S_{rxn}°}{RT_2}\right] + \left[\frac{\Delta H_{rxn}°}{RT_1} - \frac{T_1 \Delta S_{rxn}°}{RT_1}\right]$$

$$= \frac{-\Delta H_{rxn}°}{RT_2} + \frac{\Delta H_{rxn}°}{RT_1} + \frac{\Delta S_{rxn}°}{R} - \frac{\Delta S_{rxn}°}{R}$$

$$\ln \frac{K_{T_2}}{K_{T_1}} = -\frac{\Delta H_{rxn}°}{RT_2} + \frac{\Delta H_{rxn}°}{RT_1} = \frac{\Delta H_{rxn}°}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Thus, we have the following "two-point" form of the integrated van't Hoff equation, which relates our equilibrium constants and our temperature.

$$\ln \frac{K_{T_2}}{K_{T_1}} = \frac{\Delta H_{rxn}°}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Derivation of the Arrhenius Equation

Now, we can find another useful result, which is suggested by the van't Hoff equation. Since equilibrium constants are related to temperature, and equilibrium constants can be related to rate constants, we expect a similar relation for rate constants.

$$K = \frac{k_f}{k_r}$$

Thus, to derive our Arrhenius equation, which was published by Svante Arrhenius in 1889 as an empirical observation, we again begin with the Gibbs free energy.

$$\Delta G_{rxn}° = -RT \ln K$$

$$\Delta G_{rxn}° = -RT \ln \frac{k_f}{k_r}$$

Now, here is where we separate the equation.

$$G_{products}° - G_{reactants}° = -RT \ln k_f + RT \ln k_r$$

Chapter 9: Kinetics and Equilibrium Derivations

Thus, looking at the two parts to the left and the right of the equation, we can assign the Gibbs free energies to corresponding statements on the other side.

$$G_{products}° + RT \ln k_f = G_{reactants}° + RT \ln k_r$$

Since the standard Gibbs free energies for the products and reactants are all constants, and we have an equality, we can now derive our Arrhenius equation. The Arrhenius equation, according to Svante Arrhenius's experimental evidence, has the following form:

$$k = Ae^{-\frac{E_a}{RT}}$$

Where A is a constant that depends upon experimental circumstances, and E_a is the activation energy. If we take the natural logarithm of both sides, we now have:

$$\ln k = -\frac{E_a}{RT} + \ln A$$

Where $\ln A$, the natural logarithm of a constant, is just another constant. Although Arrhenius originally defined activation energy as an energy barrier that impedes reaction, the barrier is better defined as a Gibbs free energy that impedes the reaction, because reactions that are energetically unfavorable can easily occur if they are strongly entropically favored. Thus, activation energy is better expressed as activation free energy. Thus, we can separate the activation energy, into the difference between the Gibbs free energy of the substance, and the transition Gibbs free energy of reaction, which needs to be overcome for the reaction to proceed. Here, $G^{\ddagger}$ is the transition Gibbs free energy, which is greater than the standard Gibbs free energy of both the reactants and the products. Thus, subtracting the standard Gibbs free energy of reactants from the transition state Gibbs free energy yields the change in Gibbs free energy that must be associated with bringing the colliding molecules into configuration to react.

$$\ln k = -\frac{G^{\ddagger} - G_{reactants}°}{RT} + \ln A$$

$$RT \ln k = G_{reactants}° - G^{\ddagger} + RT \ln A$$

Chapter 9: Kinetics and Equilibrium Derivations

This suggests that two constants should be added to both sides of the equation relating Gibbs free energies and rate constants, for us to be able to separate the equation into the Arrhenius equation.

$$G_{products}° + RT \ln k_f + G^‡ + c_1 = G_{reactants}° + RT \ln k_r + G^‡ + c_2,$$

$$c_1 \text{ and } c_2 \text{ are constants}$$

Now, we see that we can separate these two equations. This is because the transition state Gibbs free energy is a constant, and is the same for the forward and reverse reactions. It must be surmounted by reactions going in both directions. Therefore, knowing that the standard Gibbs free energy of the products and the reactants and the transition state Gibbs free energy are all constants, we can separate the equations, due to a mathematical property of equations.

Property of equations: If A+B+C+D=E+F+G+H, where A and E are constants, then B+C+D=E, and F+G+H=A. This stems from the fact that if we have any numbers, Z+Y=W+X, if Z and W are two fixed constants, then Y must equal W, and X must equal Z. So, we now have:

$$G_{products}° = RT \ln k_r + G^‡ + c_2$$

$$G_{reactants}° = RT \ln k_f + G^‡ + c_1$$

Then, we rearrange the equation into the form of the Arrhenius equation:

$$\frac{G_{reactants}° - G^‡}{RT} = \ln k_f + \frac{c_1}{RT}$$

$$\frac{G_{products}° - G^‡}{RT} = \ln k_r + \frac{c_2}{RT}$$

Since the equation is in the form of the Arrhenius equation, and everything else is equal, we find that if c is equal to $-RT \ln A$, then what we have is the Arrhenius equation. Note that temperature generally affects both the forward and reverse rates. Therefore, as we have shown, the relation between rate constants and temperature comes from the relation between equilibrium constants and temperature. Now, that we managed to verify the Arrhenius equation, we will vary the temperature, and obtain the so-called "two-point" form of the Arrhenius equation. We again

Chapter 9: Kinetics and Equilibrium Derivations

rearrange. Here, $\Delta G^{\ddagger}$ is simply the amount of Gibbs free energy required to reach transition state, which is equal to $G^{\ddagger} - G^{\circ} = \Delta G^{\ddagger}$, and is usually similar to Arrhenius's E_a.

$$\frac{G_{reactants}{}^{\circ} - G^{\ddagger}}{R} = T_1 \ln k_{f\,T_1} + \text{constant}$$

$$\frac{G_{reactants}{}^{\circ} - G^{\ddagger}}{R} = T_2 \ln k_{f\,T_2} + \text{constant}$$

$$-\frac{\Delta G^{\ddagger}}{RT_1} = \ln k_{f\,T_1} + \text{constant}$$

$$-\frac{\Delta G^{\ddagger}}{RT_2} = \ln k_{f\,T_2} + \text{constant}$$

We subtract the two equations, which eliminates the constant, producing our final result.

$$\ln\frac{k_{f\,T_2}}{k_{f\,T_1}} = -\frac{\Delta G^{\ddagger}}{RT_2} + \frac{\Delta G^{\ddagger}}{RT_1} = \frac{\Delta G^{\ddagger}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Likewise, we get a corresponding result for the reverse rates, which is not shown, because it is of the same form. Note that we can also use the notation E_a to symbolize activation free energy, because the symbol means whatever we define it as, we can write the following:

$$\ln\frac{k_{f\,T_2}}{k_{f\,T_1}} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

And below are the more common reference table expressions for the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}}$$

$$\ln k = -\frac{E_a}{RT} + \ln A$$

Chapter 9: Kinetics and Equilibrium Derivations

Appendix A: Basic Calculus

Introduction to Calculus

To develop most of the derivations in chemistry, some basic calculus is necessary. Thus, in this portion of the text, all the methods that you may need are listed and explained. All of you guys should be familiar with the convention, that when we plot a function involving x and y on a xy graph, y is equal to f(x). Thus, I will use the two equivalently, and substitute them in for each other.

Limits: The Idea of the Very Small and Very Close

The fundamental idea of calculus is to approximate to such an accuracy that the approximation and the actual answer have no physically significant difference. The idea of getting very close to something, but not equaling that something, is expressed symbolically as a limit. The limit is basically a very precise approximation. The following notation means to approximate the value of f(x), when x is very close to the value c.

$$\lim_{x \to c} f(x)$$

For most of the time, when given a simple function, you can just substitute the value you approach for the given variable. For example, in the limit of the polynomial below, we just substitute 3 for x, and solve through:

$$\lim_{x \to 3} x^3 + 2x^2 + 4 = 49$$

Simple substitution can be done in most of the cases. Even though people like to do weird stuff in math, here we do not consider the bizarre cases that they like to talk about. This is because we are talking about chemistry, a physical science. In physical sciences, most things are well behaved. We have the constraints that the universe has set forth. Therefore, many of the cases that they study do not occur quite often. We stay physically real, so that the results we obtain are physically significant.

There are a few useful rules about limits:

1. Limits of a constant is equal to the constant:

   a. Because $x^0=1$, a constant, c, is equal to cx^0. Substituting any value into x^0 results in 1. Therefore, $\lim\limits_{x \to c} c = c$

2. Limits can be distributed in by multiplication:

   a. $\lim\limits_{x \to c}(x^2 + 5x - 2) = \lim\limits_{x \to c} x^2 + \lim\limits_{x \to c} 5x + \lim\limits_{x \to c} -2 = \lim\limits_{x \to c} x^2 + \lim\limits_{x \to c} 5x - \lim\limits_{x \to c} 2$

   b. If we really want to factor out the above, till we have it into linear factors and constants, we can go to town and do:

   c. $= \lim\limits_{x \to c} x^2 + \lim\limits_{x \to c} 5x - \lim\limits_{x \to c} 2 = \left(\lim\limits_{x \to c} x\right)\left(\lim\limits_{x \to c} x\right) + 5\lim\limits_{x \to c} x - \lim\limits_{x \to c} 2$

   d. And, applying the limit of a constant to the last term, we have:

   e. $= \left(\lim\limits_{x \to c} x\right)\left(\lim\limits_{x \to c} x\right) + 5\lim\limits_{x \to c} x - 2$

3. Limits can be factored out.

   a. We can just do the reverse of what was shown for distribution.

Weierstrass-Bolzano Epsilon-Delta Definition of the Limit

What a limit really means, is that for a function, f(x), we can make the y value as close as we want to the value we are approximating, by picking an x value that is close enough to the x value that we are approaching. Thus, it is also written in the following way, which is called the Weierstrass-Bolzano epsilon-delta definition of the limit. It is named after the two people who formulated it, and for the usage of the symbol epsilon, ϵ and delta, δ. It is in fact an inequality, which sets up a condition that tells us where we can use the limit. So, we can rewrite a limit in the form:

$$\lim\limits_{x \to c} f(x) = y, where\ c\ and\ y\ are\ constants$$

As follows:

$$\epsilon = |f(x) - y|$$

This tells us the error in the y-value we approximated, from the actual y value.

$$\delta = |x - c|$$

Appendix A: Basic Calculus

This tells us the δistance the x value we are using to estimate is from the x value we are approaching.

So, for the limit to exist, then the ε-δ definition of a limit simply requires that if we want to get closer than an error of ε to the actual y value, then we must choose an x value which is equal to or less than a value δ. If the value δ exists, where every approximation using an x value that is closer to c than δ has an error less than ε, then we can find the limit. I will now write the ε-δ definition of the limit:

$$(\forall \epsilon > 0)(\exists \delta > 0)\big((|x - c| \le \delta) \to (|f(x) - y| \le \epsilon)\big)$$

This literally reads:

$$For\ every(\forall)\ epsilon(\epsilon)\ greater\ than(>)\ zero(0)$$

$$There\ exists(\exists)\ a\ delta(\delta)\ greater\ than(>)\ zero(0)$$

The arrow indicates an if-then statement, which is called a conditional. The if and then are written before and after the arrows respectively. Looking at the if→then conditional, what is in the last parentheses reads:

$$If: we\ pick\ an\ x\ that\ is\ less\ than\ delta\ away\ from\ c$$
$$Then(\to): When\ we\ use\ that\ x\ to\ approximate, we\ will\ have\ an\ error\ less\ than\ epsilon$$

Thus, $((|x - c| \le \delta) \to (|f(x) - y| \le \epsilon))$

If these conditions which define a limit are satisfied, we can find the limit there, and the limit is said to exist. We can demonstrate this on a simple polynomial, y=2x^2+5. Polynomials are always continuous (can graph without picking up the pencil). Thus, their limits always exist, and can be found by using a x which is $0 \le \delta$ away from the x value we are approaching. Therefore, we usually just substitute in, as shown previously. However, here we are testing the epsilon-delta definition of a limit. We already know that:

$$\lim_{x \to c}(2x^2 + 5) = 2(c)^2 + 5$$

Let's say that we choose to prove that the limit exists at x equals zero. That's a good value to choose for this, because then our delta values are just going to be how far away we are from the

Appendix A: Basic Calculus

x axis. Lots of things are made substantially easier if we choose the most efficient way to calculate. This is why I chose an easy case here, because we want to show that the definition makes sense. Thus, we have:

$$\lim_{x \to 0}(2x^2 + 5) = 2(0)^2 + 5 = 5$$

From which we can find:

$$\epsilon = |x - c|$$

$$\delta = |f(x) - y|$$

Substituting in the values we just had:

$$\epsilon = |x - 0|$$

$$\delta = |f(x) - 5|$$

So, we put that into our ε-δ definition of the limit:

$$(\forall \epsilon > 0)(\exists \delta > 0)\big((|x - c| \leq \delta) \to (|f(x) - y| \leq \epsilon)\big)$$

$$(\forall \epsilon > 0)(\exists \delta > 0)\big((|x - 0| \leq \delta) \to (|(2x^2 + 5) - 5| \leq \epsilon)\big)$$

$$(\forall \epsilon > 0)(\exists \delta > 0)\big((|x| \leq \delta) \to (|2x^2| \leq \epsilon)\big)$$

From this, if we can find a relation that tells us δ based upon ε, then the limit exists. If we find the relation, we are said to have performed an epsilon-delta proof, which proves that the limit exists. In this case, we prove that the limit exists for y=2x²+5 when we approach x=0. Using the equation, y=2x²+5, we try to find the such relation. So, we do the following:

$$y = 2x^2 + 5$$

Since our if-then statement says that if $|x| \leq \delta$, then $|2x^2| \leq \epsilon$, we can solve for x, and substitute in.

$$|x| \leq \delta$$

$$|x^2| = x^2 = (|x|)^2 \; because \; squares \; of \; real \; numbers \; are \; always \; positive$$

Thus

Appendix A: Basic Calculus

$$x^2 \leq \delta^2$$

Substituting in δ^2 for x^2, we have:

$$y = 2x^2 + 5 \leq 2\delta^2 + 5$$

The reason y is less than or equal to the result of the substitution is because what we substituted in on the right side for x^2 is greater than or equal to x^2. Thus, in this case, y is less than or equal to the substituted statement. For now, we move on to the delta. We do the same for our epsilon:

$$|2x^2| \leq \epsilon$$

Because the two is positive, we are allowed to take it out from the absolute value.

$$2|x^2| \leq \epsilon$$

Likewise, the same applies for the x^2, because it is also positive:

$$2x^2 \leq \epsilon$$

Dividing both sides by 2 allows us to find something we can substitute in:

$$x^2 \leq \frac{\epsilon}{2}$$

So, we substitute in $\frac{\epsilon}{2}$ for x^2:

$$y = 2x^2 + 5 = \frac{2\epsilon}{2} + 5 = \epsilon + 5$$

The reason why we substitute in an equality, is because we CHOOSE the arbitrary epsilon. So, we know how big epsilon is. Then, solving with the equation, we know the error exactly, and the x value deviation required to produce the error.

Now, we have two statements involving y, with an epsilon in one, and a delta in the other. Combining the two allows for us to relate epsilon to delta, and complete the proof.

$$y \leq 2\delta^2 + 5$$

$$y = \epsilon + 5$$

Appendix A: Basic Calculus

Since the right side of the first statement is greater than y, and the right side of the second statement is equal to y, combining the two results in what we wanted:

$$\epsilon + 5 \le 2\delta^2 + 5$$

This relates our epsilon to our delta, and we are almost done with our proof. We can further simplify it for demonstration purposes:

Subtracting 5 from both sides:

$$\epsilon \le 2\delta^2$$

$$\frac{\epsilon}{2} \le \delta^2$$

This gives us our condition that must be satisfied, for our limit of $y=2x^2+5$ to exist around x=0. Indeed, testing a couple of values, we find it to be valid, and thus the limit exists for $2x^2+5$ at x=0. What this inequality literally means is that half of the error of the approximation, $\frac{\epsilon}{2}$, is less than the square of the distance between the value we use to approximate and the x value we are approaching, δ^2. Furthermore, we can rearrange the equation, so that for every epsilon, we can find the maximum delta. We result in:

$$\delta \ge \sqrt{\left(\frac{\epsilon}{2}\right)}$$

Therefore, for the function $f(x)=2x^2+5$, and with the x value we are approaching as zero, if we want the maximum delta that produces an error less than the epsilon we choose, we have:

$$\delta_{max} = \sqrt{\left(\frac{\epsilon_{desired}}{2}\right)}$$

When we use this result, we choose the accuracy we desire and set epsilon to a fixed value. Then, we calculate the maximum delta, or distance between the x value we use to approximate, and the x value that we are approaching. Note that we only result in a positive square root, because epsilon and delta are defined to be equal to absolute values, and absolute values are always positive. Here, the inequality means that the square root of half of the error is less than or equal to delta. Thus, for example, if we want to have an error of less than 50 in this case, we do:

Appendix A: Basic Calculus

$$\delta_{max} = \sqrt{\left(\frac{\epsilon}{2}\right)}$$

$$\delta_{max} = \sqrt{\frac{50}{2}} = \sqrt{25} = 5$$

Thus, we find that if our delta is less than 5, the error will be less than 50

$$Because \ \sqrt{\left(\frac{\epsilon}{2}\right)} \leq \delta$$

$$and \ \delta_{max} = 5 \ for \ \epsilon \leq 50$$

$$if \ \delta \leq \delta_{max} \rightarrow \epsilon \leq 50$$

Likewise:

$$If: |x - c| \leq \delta_{max}$$
$$Then: |f(x) - y| \leq \epsilon$$

And in this case:

$$When \ c = 0, f(x) = 2x^2 + 5, \delta = 5, \epsilon = 50, and \ y(0) = 5$$
$$If: |x| \leq 5$$
$$Then: |f(x) - 5| \leq 50$$

$$Or, in \ symbolic \ notation, (|x| \leq 5) \rightarrow (|f(x) - 5| \leq 50)$$

Equivalently, we can say that:

$$If: (c - \delta) \leq x \leq (c + \delta)$$
$$Then: -\epsilon \leq f(x) - f(c) \leq \epsilon$$

$$Likewise, \left((c - \delta) \leq x \leq (c + \delta)\right) \rightarrow (-\epsilon \leq f(x) - f(c) \leq \epsilon)$$

And since:

$$(|x| \leq 5) \rightarrow (|f(x) - 5| \leq 50)$$
$$And \ c = 0, f(x) = 2x^2 + 5, \delta = 5, \epsilon = 50, and \ y(0) = 5$$

Appendix A: Basic Calculus
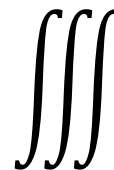
$$If: (0 - 5) \le x \le (0 + 5)$$
$$Then: -50 \le f(x) - y(0) \le 50$$
$$(-5 \le x \le 5) \to (-50 \le f(x) - y(0) \le 50)$$

Epsilon-delta proofs for the existence of a limit are usually applied to specific cases, and are often used to show that a limit does or does not exist. Take, for example, a vertical line. Even if delta is equal to zero, we cannot possibly make the y value of the vertical line always less than any epsilon that we choose, because vertical lines have y values that extend to infinity. Infinity is not a number, and thus cannot be used as an epsilon. Thus, with only words, and 3 sentences, we just proved that limits of vertical lines do not exist. However, do note that vertical lines are not really found in real life, because again, there is such a thing as time. These proofs get hard in mathematics, but are very rare in the basic sciences. The only thing important is that they show that a function approaches a y value when we approach an x value. The reason why it is discussed here, is because the idea of approaching is very important to proofs, derivatives, and integrals.

Derivatives and integrals are exact in limiting cases, meaning that they become exact as something approaches a value. Derivatives become exact, when the small change in x becomes essentially zero (When we do a slope over an interval that is nearly zero, we closely approximate the slope of a point in that tiny interval. Note that later we will see that the small change in x never equals zero, because that will result in division by zero). Integrals become exact, when the areas we are summing get close to zero, or when the number of subdivisions that we make in the area we are finding becomes close to infinity (When the areas we are summing get close to zero, the error that results from summing gets close to zero. Since the error becomes closer to zero faster than the areas we are summing, if we make the areas we are summing essentially almost equal to zero, then we have virtually no error at all. This is the same as cutting the area into nearly an infinite number of pieces, which makes the pieces very small).

Appendix A: Basic Calculus
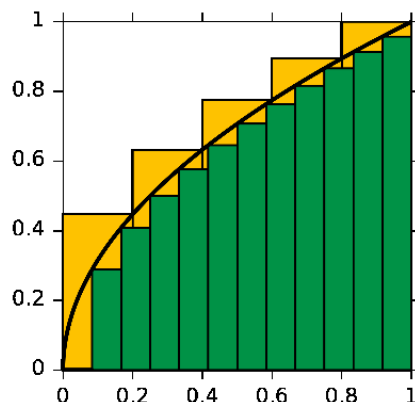
Figure A.1. When the area underneath a curve is approximated using smaller and smaller pieces, the error decreases.

Derivatives: The Idea of Slope

Many times, we must find the slope of something. The average slope of something is given by a familiar formula, as shown below:

$$\frac{\Delta y}{\Delta x} = \frac{\Delta[f(x)]}{\Delta x} = \text{average slope}$$

However, say we want to find the slope of a function at a given point. Then, we seemingly run into a problem, because the above formula requires an interval, and intervals are made up of many points. But, the problem is escaped by inching closer and closer and closer to the point, so that the change in x, Δx, is virtually zero. That means that the slope that we find is very close to the slope of the function at a single point, which is synonymous with finding the tangent to the curve at that point.

Appendix A: Basic Calculus
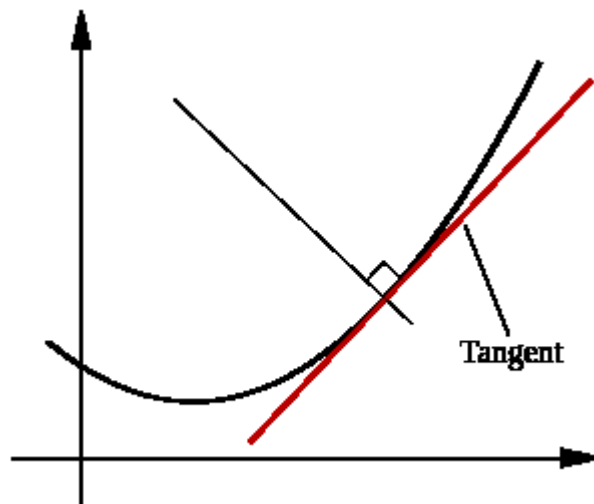
Figure A.2. The slope of a curve at a point is equal to the slope of the tangent line to the curve at that point. The derivative gives us a function to allow for us to find the slope of another function at any given x value.

When we do so, we change notation. Instead of $\frac{\Delta y}{\Delta x}$, we write $\frac{dy}{dx}$. The d just means a very small change in the variable that follows it. Thus, the d is just a very small delta, so small that the function is nearly a straight line over the interval x to x+dx. Therefore, the following equation, is the slope of the function at a single point:

$$\frac{dy}{dx} = \frac{d[f(x)]}{dx} = slope\ at\ a\ single\ point$$

$\frac{dy}{dx}$ is called the derivative of the function y with respect to x. The process of finding $\frac{dy}{dx}$ is called differentiation. It literally means "the very small change in y caused by a very small change in x", dy, divided by "the very small change in x", dx. This is equal to the slope over a very small interval, which is approximately equal to the slope of the function at (x,y). Thus, if we replace the d's with deltas, we just get the slope formula. The derivative is just the function that gives the slope of another function, and it means that at a given point (x,y), a small change in x, dx, causes a small change in y, dy. We can also write:

$$dy = \frac{dy}{dx}dx$$

Which reads that the very small change in y, dy, is equal to the derivative of the function at (x,y) multiplied by a very small change in x, dx. Cancelling dx on the right side indeed results in dy.

Appendix A: Basic Calculus

This is a differential equation. A differential equation means that a very small change in x, dx, causes a very small change in y, dy. When we add up all the dy's, we get Δy. This allows us to find an equation that has a derivative of $\frac{dy}{dx}$, which is what integration is all about. The differential equation will be used when we integrate, and we will see that later.

The Limit Definition of the Derivative

To obtain a function that describes $\frac{dy}{dx}$ at every point of the function y, we need to do $\frac{dy}{dx}$ for every point of the function.

$$\frac{f(x+\Delta x)-f(x)}{\Delta x} = \frac{\Delta y}{\Delta x} \qquad \text{Therefore} \qquad \frac{dy}{dx} = \lim_{\Delta x \to 0} \frac{f(x+\Delta x)-f(x)}{\Delta x}$$
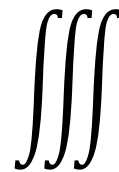
The limit makes the delta x become dx, because it forces the change in x to be very small. Since the function does not change much if there is only a small change in x, it forces the change in y to be small as well. So, we write dy. To find the average slope, $\frac{\Delta y}{\Delta x}$, between two points x and x+Δx, we evaluate the function at x+Δx, subtract the function evaluated at x, and then divide by the difference in x for the two points, which is just Δx. However, to find the slope at a single given point, $\frac{dy}{dx}$, notice that limit in front. This means that the two points, x+Δx and x are separated only by a very small Δx that is approximately zero. Thus, the two points are right next to each other on the graph, and doing the slope formula on them will provide a very good approximation of the slope of the function at point x. Since dy/dx is the derivative, we write the derivative of something as:

$$\frac{dy}{dx} \text{ of } (y = \text{something}) = \frac{d(\text{something})}{dx}$$

Thus, we just substitute the function in for y.

Properties of d/dx

One important property of the differential operator, $\frac{d}{dx}$, which takes the derivative of whatever follows it, is that it can be distributed into a parenthesis by multiplication. Thus,

Appendix A: Basic Calculus

$$\frac{dy}{dx} \text{ where } y = 3x^2 + 2x + 7 = \frac{d(3x^2 + 2x + 7)}{dx} = \frac{d(3x^2)}{dx} + \frac{d(2x)}{dx} + \frac{d(7)}{dx}$$

Also, it can be distributed through a constant:

$$\frac{d(3x^2)}{dx} + \frac{d(2x)}{dx} + \frac{d(7)}{dx} = \frac{d(x^2 + x^2 + x^2)}{dx} + \frac{d(x + x)}{dx} + \frac{d(7)}{dx}$$

$$= \frac{d(x^2)}{dx} + \frac{d(x^2)}{dx} + \frac{d(x^2)}{dx} + \frac{d(x)}{dx} + \frac{d(x)}{dx} + \frac{d(7)}{dx} = 3\frac{dx^2}{dx} + 2\frac{d(x)}{dx} + \frac{d(7)}{dx}$$

However, do note that we cannot distribute further, and below we see that most common errors are due to mathematical mistakes.

$$\frac{d[x^2]}{dy} = \frac{d(x * x)}{dy} \text{ does NOT equal any of the following: } \frac{dx * dx}{dy}, 2\frac{dx}{dy}, \frac{dx}{dy}\frac{dx}{dy}, \frac{(dx)^2}{(dy)^2}, \frac{d^2x^2}{d^2y^2}$$

We continue onwards, to the derivatives of powers of x:

Derivatives of Powers of x

The derivative of a constant function is always zero, because we get horizontal lines when we graph constants, and horizontal lines have a slope of zero. We can write constants as a constant c, multiplied by $x^0=1$. Thus, the 3 was just $3x^0$. Below, we demonstrate that differentiating, or taking the derivative of y=c, where c is a constant, produces 0. The reason why we write cx^0 will be explained later.

$$\frac{dy}{dx} of\ y = cx^0$$

$$\frac{dy}{dx} = \lim_{\Delta x \to 0} \frac{y(x + \Delta x) - y(x)}{\Delta x} = \lim_{\Delta x \to 0} \frac{c(x + \Delta x)^0 - cx^0}{\Delta x} = \lim_{\Delta x \to 0} \frac{c(1) - c(1)}{\Delta x} = \lim_{\Delta x \to 0} \frac{0}{\Delta x} = 0$$

Thus, we just showed that our formula for dy/dx produces zero for any constant.

$$\frac{dy}{dx} = \frac{d(c)}{dx} = 0\ where\ y = cx^0 = c$$

Appendix A: Basic Calculus

We move on, from a constant, to a constant multiplied by x. Since a constant multiplied by c yields a line, and lines have a constant slope, we expect to get a constant. And, since lines can be written as y=cx+b, where c and b are constants, they simply have derivatives which equal their constant slope, c. Therefore, we expect to get the constant c. Note that the b does not matter, because when we distribute we get the following, which includes the derivative of a constant, which is zero.

$$\frac{dy}{dx} \text{ where } y = cx + b = \frac{d(cx+b)}{dx} = \frac{d(cx)}{dx} + \frac{d(b)}{dx} = \frac{d(cx)}{dx} + 0 = \frac{d(cx)}{dx} = c$$

To prove the above, we use the limit definition of a derivative:

$$\frac{dy}{dx} = \frac{d(cx)}{dx} \text{ when } y = cx^1 + bx^0$$

$$\frac{dy}{dx} = \lim_{\Delta x \to 0} \frac{y(x + \Delta x) - y(x)}{\Delta x} = \lim_{\Delta x \to 0} \frac{c(x + \Delta x)^1 - cx^1}{\Delta x} = \lim_{\Delta x \to 0} \frac{cx + c(\Delta x) - cx}{\Delta x}$$

$$= \lim_{\Delta x \to 0} \frac{c(\Delta x)}{\Delta x} = \lim_{\Delta x \to 0} c = c, \text{ because the limit of a constant is the constant itself}$$

Note that we could have just factored out the constant c, and did the following:

$$\frac{dy}{dx} = \lim_{\Delta x \to 0} \frac{y(x + \Delta x) - y(x)}{\Delta x} = c \lim_{\Delta x \to 0} \frac{(x + \Delta x)^1 - x^1}{\Delta x} = c \lim_{\Delta x \to 0} \frac{x + (\Delta x) - x}{\Delta x}$$

$$= c \lim_{\Delta x \to 0} \frac{(\Delta x)}{\Delta x} = c \lim_{\Delta x \to 0} 1 = c(1) = c$$

Thus, we have shown:

$$\frac{dy}{dx} = \frac{d(cx)}{dx} = c \text{ when } y = cx^1 + bx^0$$

And note that we indeed obtained a constant slope of c for the line.

Now, we move to cx^2, and do the same. However, note that we cut out the terms after cx^2, because we know how to find their derivatives after we multiply in the dy/dx.

$$\frac{dy}{dx} = \frac{d(cx^2)}{dx} \text{ when } y = cx^2$$

Appendix A: Basic Calculus

$$\frac{dy}{dx} = \lim_{\Delta x \to 0} \frac{y(x + \Delta x) - y(x)}{\Delta x} = \lim_{\Delta x \to 0} \frac{c(x + \Delta x)^2 - cx^2}{\Delta x}$$

$$= \lim_{\Delta x \to 0} \frac{cx^2 + c2x(\Delta x) + c(\Delta x)^2 - cx^2}{\Delta x}$$

$$= \lim_{\Delta x \to 0} \frac{c2x(\Delta x) + c(\Delta x)^2}{\Delta x} = \lim_{\Delta x \to 0} c2x + c\Delta x = c2x + c(0) = c2x$$

Notice that in the last line, we just substitute in 0 for Δx. By then, it is okay, because Δx is no longer in the denominator. If we substitute in earlier, we get 0/0, which is an indeterminant form. That is bad. Very bad. Chemists do not like that kind of complicated math stuff. We use computers to do that for us instead. Likewise, we could have pulled out the c, and did:

$$c \lim_{\Delta x \to 0} \frac{(x + \Delta x)^2 - x^2}{\Delta x}$$

Which results in the same thing, because limits can be distributed in by multiplication. Thus, we confirmed that:

$$\frac{dy}{dx} = \frac{d(cx^2)}{dx} = c2x \text{ where } y = cx^2$$

By now, with three examples of derivatives of the form d(cx^n)/dx, where c and n are constants, follow a pattern. In math, we have to be careful when jumping to conclusions. Although our brain screams pattern after three occurrences, there are many examples of things that seem to follow a pattern but later fail to follow the pattern. Math requires proofs. However, this is not a calculus book, so I will tell you that there is a pattern. When we repeat the same process for cx^3, cx^4, cx^n, we get $3cx^2$, $4cx^3$, and so forth. This pattern also holds for negative and fractional powers. Cut to the chase, below is the power rule which can be used when we have a cx^n where c and n are constants. The reason it is called the power rule is because the x is raised to a fixed power.

The Power Rule:
$$\frac{dy}{dx} = \frac{d(cx^n)}{dx} = c\frac{d(x^n)}{dx} = cnx^{n-1} \text{ When } y = cx^n, \text{ and } c, n \text{ are constants}$$

Appendix A: Basic Calculus

With that, we can differentiate any polynomial. However, note that we cannot get $\frac{1}{x} = x^{-1}$, because the derivative of a constant, which involves x^0, results in 0. Thus, this is a special case, which will be revisited later.

When we have multiple terms, we are allowed to take the function, differentiate each term, and then put it back together, because we can multiply the d/dx through parentheses, as we demonstrated earlier. It makes sense, because the change in the entire function is equal to the change in each term added together. Therefore, differentiating each of the terms and adding them together provides a correct result.

Other Rules

We have two more rules, that are sometimes useful. The product rule is applied when you have a function multiplied by another function. For example, the derivate of f(x)z(x) where f(x) and z(x) are functions of x, which is $\frac{\mathrm{d}[f(x)z(x)]}{\mathrm{d}x}$, is insanely hard if the product of f(x) and z(x) is not easy to differentiate (aka not a polynomial or something like that). We then we apply the product rule:

$$\frac{\mathrm{d}[f(x)z(x)]}{\mathrm{d}x} = f(x)\frac{\mathrm{d}[z(x)]}{\mathrm{d}x} + z(x)\frac{\mathrm{d}[f(x)]}{\mathrm{d}x}$$

This should be pretty self-explanatory.

The Chain Rule

The last rule that is useful, especially when writing proofs, is the chain rule. The chain rule is applied when we have a function that relies on another function. It is commonly written as:

$$\frac{\mathrm{d}[f(z(x))]}{\mathrm{d}x} = \frac{\mathrm{d}[f(z(x))]}{\mathrm{d}[z(x)]} * \frac{\mathrm{d}[z(x)]}{\mathrm{d}x}$$

To use the formula, it is very helpful to think of the formula in the following way:

Appendix A: Basic Calculus

$$\frac{d\big(f(s)\big)}{dx} = \frac{df(s)}{ds} * \frac{d(s)}{dx} \quad \text{when } s \text{ is a function of } x$$

Thus, setting s=z(x), we get the following:

$$\frac{df\big(z(x)\big)}{dx} = \frac{d\big(f(s)\big)}{dx} = \frac{df(s)}{ds} * \frac{d(s)}{dx} \text{ where } s = z(x)$$

Thus, we differentiate z(x) the normal way, and differentiate f(s) just like how we differentiate f(x), except that s goes in the place where the x normally is. Then, substituting back in

$$z(x) \text{ for } s, \text{ and } \frac{d\big(z(x)\big)}{dx} \text{ } for \text{ } \frac{d(s)}{dx}$$

We get the original

$$\frac{df\big(z(x)\big)}{dx} = \frac{df(z(x))}{d(z(x))} * \frac{d\big(z(x)\big)}{dx}$$

The chain rule can also be written as:

$$\frac{dy}{dx} = \frac{dy}{dz} * \frac{dz}{dx}$$

Note that cancelling out the dz on the right-side results in dy/dx. The equation literally reads: "a small change in y due to a small change in x", dy, divided by "the small change in x", dx, is equal to "a small change in y due to a small change in z due to a small change in x", dy, divided by "the small change of z due to a small change in x", dz, multiplied by "the small change in z due to a small change in x", dz, and then finally divided by "the small change in x". Note that multiplying then dividing by dz results in multiplying by 1, thus leaving only dy/dx. This means that we find the slope of y with respect to z, and then use the slope of z with respect to x to find the slope of y with respect to x. The chain rule is hard to explain without an example. So, we have the following:

Example Using the Chain Rule:
$$y = (3x)^3 = (z(x))^3 \text{ where } z(x) = 3x$$

$$= f(z(x)) \text{ where } f(s) = s^3$$

Appendix A: Basic Calculus

$$= f(z(x)) \text{ where } s = z(x)$$

For the derivative, substituting in f(s) and z(x), we get

$$\frac{dy}{dx} = \frac{d((3x)^3)}{dx} = \frac{d\left((z(x))^3\right)}{dx} = \frac{d\left(f(z(x))\right)}{dx}$$

Then, we find that:

$$\frac{d(f(s))}{ds} = \frac{d(s^3)}{ds} = 3s^2 \text{ and that } \frac{d(s)}{dx} = \frac{d(z(x))}{dx} = \frac{d(3x)}{dx} = 3$$

Thus, substituting into our previous formula,

$$\frac{df(z(x))}{dx} = \frac{df(z(x))}{d(z(x))} * \frac{d(z(x))}{dx} = \frac{df(s)}{ds} * \frac{d(s)}{dx}$$

We get:

$$\frac{df(s)}{ds} * \frac{d(s)}{dx} = 3(s^2) * 3 = 3(3x)^2 * 3 = 81x^2$$

And indeed, we find the same result if we expanded the right side of y=(3x)³:

$$y = 27x^3, \text{using the power rule,} \frac{dy}{dx} = \frac{d(27x^3)}{dx} = 27\frac{d(x^3)}{dx} = 27 * 3 * x^2 = 81x^2$$

Although these rules seem useless now, we will encounter them again later.

Integration: Adding Up Parts to Make a Whole

If we take an average slope, and multiply by the change in x, we get the change in y.

$$\frac{\Delta y}{\Delta x} * \Delta x = \Delta y$$

Appendix A: Basic Calculus
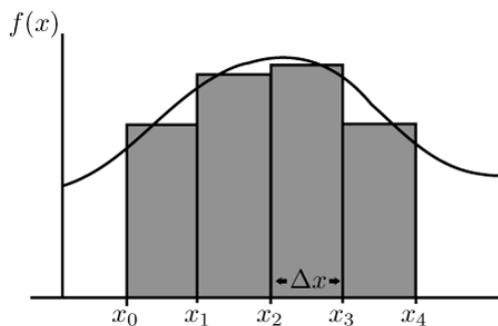
Figure A.3. If the curve represents the slope of another function, then multiplying a point on the curve, (dy/dx), by the interval size of x, (dx), and then adding up the pieces, allows for us to find the approximate value of the function that produced the slope curve. Thus, to find the original function, we add up the area underneath its derivative.

Same applies if we take our small little slopes and multiply them by the small little changes in x.

$$\frac{dy}{dx} * dx = dy$$
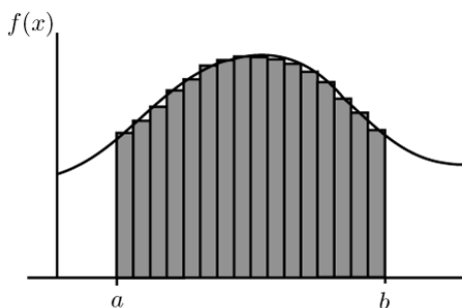
Figure A.4. As we cut the area under the graph into more and more pieces, we get better and better approximations. When the number of subdivisions becomes infinite, the error essentially becomes zero, and we get the area underneath the curve which we want by summing up all the little slices.

When the number of subdivisions become infinite, we have pretty much the exact amount of area underneath the curve.

Appendix A: Basic Calculus

The Definite Integral

Here is where that differential equation way of writing the derivative comes in handy. It gives a graphical idea of $\frac{dy}{dx}$. We find that $\frac{dy}{dx}dx$ simply means the small amount of area contained between the graph of the derivative of the function y and the x-axis, and the two vertical lines x=x₁ and x=x₂=x+dx. To find the change in the original function from x₁ to x₂, we find the area beneath the graph of the derivative of y(x) from x₁ to x₂. This is the graphical approach to integration. To find that area, we just add up all the $\frac{dy}{dx}dx$'s. To add up these tiny little bars, we just do a sum. The integral symbol, ∫, means to sum up all the little sections that we get from multiplying $\frac{dy}{dx}$ by dx. It used to be an elongated S which stood for sum. It also means to add up all the dy's, which is equal to adding up all the little m(x)dx's, which results in a Δy value. When integrating polynomials, we can integrate the individual terms and add them up in the end, just like how we differentiate. Thus, integration can also be distributed by multiplication through parentheses. So, to sum up all the dy=$\frac{dy}{dx}dx$'s, from x₁ to x₂, we write:

$$\Delta y_{x_1 to x_2} = \text{area under the derivative from } x_1 \text{ to } x_2 = \int_{x_1}^{x_2} dy = \int_{x_1}^{x_2} \frac{dy}{dx} dx = \text{a number}$$

For every equation we encountered so far, we have found that $\frac{dy}{dx}$ = another function, which we will call m(x). To get what we have above, we can just do the following:

$$\frac{dy}{dx} = m(x)$$

$$dy = m(x)dx$$

$$\Delta y_{x_1 to x_2} = \text{area under } m(x) \text{ from } x_1 \text{to } x_2 = \int_{x_1}^{x_2} dy = \int_{x_1}^{x_2} \frac{dy}{dx} dx = \int_{x_1}^{x_2} m(x)\,dx$$

$$= \text{a number}$$

This is known as the definite integral, because we get a definite numerical answer. The x_1 and x_2 are known as limits of integration.

Appendix A: Basic Calculus

Loss of a Constant Due to Differentiation

Differentiating g(x)+k, where k is a constant, gives the same result as differentiating g(x), because the derivative of a constant is a constant. Therefore, we lose the constant when we integrate. Thus, if we do not know the original constant, or a point on the original function, we do not yet know the original function. We only know the form of a family of functions that all give the same derivative. Thus, we have the following, where c is any constant. Note that the x_1 and the x_2 are missing. This means that we are finding the exact value of y for any given x, which is a function.

$$\int dy = \int \frac{dy}{dx}dx = \int m(x)dx = y = \text{a function}, y(x) + c$$

Note that we can assign any value to c, and since the derivative of a constant is a constant,

$$\frac{d(y(x) + c)}{dx} = \frac{d(y(x))}{dx} = \frac{dy}{dx} = m(x)$$

Here I bring to your attention, that when we wrote y in the past, we meant y(x). However, when we wrote x, we automatically assumed that x is a variable. For many things in chemistry, although they are written as a single letter, they are actually a function! For example, for an ideal gas, p (pressure) is a function of n (amount of gas), T (temperature), and V (volume), so p is a function of n, T, and V, and can be written as $p(n, T, V)$. You must be a little careful in chemistry, because chemistry is partly the study of relations, and very often a rather complex fraction is assigned a single-letter variable. Back to the point.

Since there is an infinite number of c's, there are an infinite number of functions in the family y(x)+c, all of which satisfy $\frac{dy(y(x)+c)}{dx} = \frac{d(y(x))}{dx} = \frac{dy}{dx} = m(x)$, we need more information to know the original function, y(x), such as the value of the constant, or a point on the original function. The loss of a constant is illustrated below, followed by an example of recovering the constant based upon additional information.

The Power Rule

The power rule for integration is the reverse of the power rule for differentiation. However, whenever we integrate, we add a constant. That will be explained after the example.

Appendix A: Basic Calculus

Power rule for integration:

$$\int kx^n \, dx = k\frac{x^{n+1}}{n+1} + c, \text{where } k, n, c \text{ are constants}$$

However, because the power rule for integration cannot be applied for the special case of x^{-1}, because x^{-1} cannot be produced by the derivative power rule. Thus, the reverse of the derivative power rule, the integration power rule, does not hold for this case. We will figure out how to integrate that later. For now, consider the following example:

For example: for $y = 5x^3 - 7x^2 + 3$:

$$\frac{d[5x^3 - 7x^2 + 3]}{dx} = \frac{d[5x^3]}{dx} - \frac{d[7x^2]}{dx} + \frac{d[3]}{dx} = 15x^2 - 14x + 0$$

Therefore, applying the rule provided above,

$$\frac{dy}{dx} = 15x^2 - 14x \text{ thus } dy = (15x^2 - 14x)dx = 15x^2 dx - 14x dx$$

And

$$\int dy = y + c = \int (15x^2 - 14x)dx = \int 15x^2 dx + \int -14x dx = 15 \int x^2 dx - 14 \int x dx$$
$$= 5x^3 - 7x^2 + c$$

You may think, where did the 3 go? And what is the c? Well, that c, which is a constant, is the 3. However, many times, we will not know the original function. Therefore, to find the original function, we either need to be given the original constant, or most often, a point on the graph of the original function, y(x). If neither the original function, y(x), nor the constant was given, and instead I gave you the point (1,2), then you would likewise be able to find that c is equal to 3. You can do

$$y(1) = 2 = 5(2)^3 - 7(2)^2 +, and \text{ solving for } c, c = -10$$

The problem occurs, because when we differentiate a constant, we get zero. Thus, y, y+1, y+1000, y+ any constant, would always yield the same thing. However, when we integrate, we do not know the constant, because differentiation causes a loss of information. Therefore, if we

Appendix A: Basic Calculus

want to know the original function, we reintroduce the constant afterwards. When we want the original function, all we do is

$$y + c = \int dy = \int \frac{dy}{dx} dy = \int m(x) dx$$

And then, using additional information, we can find the constant, c. We obtain the indefinite integral by integrating without the limits of integration. The integral is indefinite because we do not know the definite value of the constant. However, from the definite integral, it is very easy to find the indefinite integral, which includes the limits of integration.

Return of the Limit

Definite integrals, which have limits, x_1 and x_2, produce a definite value. Now, you may ask, why do we get an exact value for the integrals with limits? Notice that what we are finding in that case is Δy from x_1 to x_2. This is a change, which is equal to a difference. Whenever we find a difference, we subtract. Thus,

$$\Delta y_{x_1 \, to \, x_2} = \text{area under} \left(m(x) = \frac{dy}{dx} \right) \text{ from } x_1 \text{ to } x_2 = \int_{x_1}^{x_2} dy = \int_{x_1}^{x_2} \frac{dy}{dx} dx = \int_{x_1}^{x_2} m(x) \, dx$$

Simply means find the area under m(x)=dy/dx from x=0 to x_2, and subtract from that, the area under m(x)=dx/dy from x=0 to x_1. Thus,

$$\Delta y_{x_1 \, to \, x_2} = \int_{x_1}^{x_2} dy = \int_{x_1}^{x_2} \frac{dy}{dx} dx = \int_{x_1}^{x_2} m(x) \, dx$$

Can be rewritten as:

$$\Delta y_{From \, x_1 \, to \, x_2} = \Delta y_{x=0 \, to \, x_2} - \Delta y_{x=0 \, to \, x_1}$$

$$= \int_{x=0}^{x_2} dy - \int_{x=0}^{x_1} dy = \int_{x=0}^{x_2} \frac{dy}{dx} dx - \int_{x=0}^{x_1} \frac{dy}{dx} dx = \int_{x=0}^{x_2} m(x) \, dx - \int_{x=0}^{x_1} m(x) \, dx$$

Since we see that the integrals are from x=0 to some x, we can replace the integrals as such:

$$\int_{x=0}^{x_1} \frac{dy}{dx} dx = (y(x) + c)|_{x=0}^{x_1} = \int_{x=0}^{x_1} m(x) \, dx$$

Appendix A: Basic Calculus

Now, you may be unfamiliar with the | notation. However, that just means to do the following:

$$(y(x_1) + c) - (y(0) + c) = (y(x) + c)|_{x_1} - (y(x) + c)|_{x=0} = (y(x) + c)|_{x=0}^{x_1}$$

Note that here, x_1 is a value. Thus, the bar with a variable equals a variable simply means to evaluate whatever that is before the bar when the variable next to the bar is equal to the value. We do this by substituting the variable for what we define the variable to be equal. When we have a variable and a value subscripted, and a value subscripted, then we just evaluate what came before the bar for the superscripted value, and subtract from that the same function evaluated for the subscripted value. Note that we do not need to write x= twice, because by writing it once, we imply that the second value given is for the same variable we are talking about. Note that we can also use any constant, instead of the zero, because all possible overlap cancels out. However, observe the c closely. The c cancels out, because when we do the subtraction, we get:

$$y(x_1) - y(0) + c - c = y(x_1) - y(0) = \Delta y_{from\ x=0\ to\ x=x_1}$$

Thus, we do get a difference, that is equal to the change of some function from zero to a value, x, that we plug in. So, we just found y(x)+k, just like in the case of the indefinite integral. However, when we do the definite integral, we take y(x)+k evaluated at some x_2, and subtract from it y(x)+k evaluated at some x_1, where x_1 and x_2 are constants, which just results in y(x) evaluated at x_2 minus y(x) evaluated at x_1, because the constants cancel. Because the constant cancels, we can evaluate definite integrals, without knowing the value of the constant.

$$\Delta y_{from\ x=x_1\ to\ x=x_2} = \int_{x=0}^{x_2} dy - \int_{x=0}^{x_1} dy = (y(x_2) + k) - (y(x_1) + k) = y(x_2) - y(x_1)$$

$$= \int_{x=0}^{x_2} \frac{dy}{dx} dx - \int_{x=0}^{x_1} \frac{dy}{dx} dx = \int_{x=0}^{x_2} m(x)\, dx - \int_{x=0}^{x_1} m(x)\, dx$$

Notice, that this just equal to evaluating an indefinite integral at two x values, and then taking the indefinite integral evaluated at the larger x value, and subtracting from it the same indefinite integral evaluated at the smaller x value. Note, however, the constant c must be the same in both cases, because we are using the same indefinite integral. If we use a different constant, we get an incorrect result, because the constants do not cancel each other if they are not the same.

Appendix A: Basic Calculus

Thus:

$$\Delta y_{from\ x=x_1\ to\ x=x_2} = \int_{x_1}^{x_2} dy = \int_{x_1}^{x_2} \frac{dy}{dx} dx$$

$$= \int_{x=0}^{x_2} dy - \int_{x=0}^{x_1} dy = \int_{x=0}^{x_2} \frac{dy}{dx} dx - \int_{x=0}^{x_1} \frac{dy}{dx} dx =$$

$$= \int \frac{dy}{dx} dx \,|_{x=x_2} - \int \frac{dy}{dx} dx \,|_{x=x_1}$$

$$= (y(x) + c)|_{x=x_2} - (y(x) + c)|_{x=x_1}$$

$$= (y(x_2) + c) - (y(x_1) + c) = y(x_2) - y(x_1)$$

It is a common practice to find the definite integral in this fashion. The reason why we do this, is because we find a y(x)+c anyways when we evaluate a definite integral. Thus, we find that it is impossible to find the original function if we are not given anything but the derivative, but we can still find the change in the original function.

The Fundamental Theorem of Calculus, its Corollary, and the Newton-Leibniz Axiom

The Fundamental Theorem of Calculus

Without even saying it, I just introduced you to the Fundamental Theorem of Calculus, its corollary, and the Newton-Leibniz axiom (sometimes called the second part to the Fundamental Theorem of calculus, its formulation marked the discovery of calculus). The fundamental theorem of calculus says that if you differentiate a function, you get its derivative and lose the constant. Then, when you find the indefinite integral, you get the same function, plus a constant c. Thus, integrating a function sometimes is called finding the antiderivative, and any antiderivative satisfies the differential equation we obtained by differentiating. Thus, the family of functions that we talked about, y(x)+c, where c is any constant, and dy/dx equals the derivative before, is simply the family of antiderivatives. Note that for a function, there are an infinite number of antiderivatives, and to find the original function, which is an antiderivative, additional information must be provided. Thus, the fundamental theorem of calculus, is just what we had before:

Appendix A: Basic Calculus

$$dy = \frac{dy}{dx}\,dx$$

$$\int dy = \int \frac{dy}{dx}\,dx = y(x) + c$$

And, likewise:

$$\frac{d(y(x) + c)}{dx} = \frac{d\big(y(x)\big)}{dx} = \frac{dy}{dx}$$

Note that we can also do the following:

$$dy = \frac{dy}{dx}\,dx$$

$$\int dy = \int_{x=0}^{x} \frac{dy}{dt}\,dt = y(x) + c$$

Note that by simply changing the variable, we get a function instead. This is an indefinite integral! Thus, an easy way to tell definite integrals from indefinite integrals is to look at the limits. Note that in a definite integral, the limits are two constants. However, in the indefinite integral, there is a variable as a limit. Also, note that in indefinite integrals, the variable that we have as the limit cannot be the same variable as in the differential equation. This is because this "index" variable matters, and we get errors if the variable found in the limit is the same as one of the variables in the differential equation, or one of the variables in the original equation. Since when we evaluate an equation, we get a constant, the limit that is a constant in the indefinite integral can equal any constant, because we can simply compensate by changing the constant c accordingly. Thus, we can do the following:

$$\int dy = \int_{x=k}^{x} \frac{dy}{dt}\,dt = y(x) + c, \text{where } k \text{ is a constant, and } c \text{ is a constant}$$

The Corollary to the Fundamental Theorem of Calculus:

For a derivative:

$$dy = \frac{dy}{dx}\,dx$$

Appendix A: Basic Calculus

$$\Delta y_{from\ x=x_1\ to\ x=x_2} = \text{area under } \left(m(x) = \frac{dy}{dx} \right) \text{ from } x_1 \text{ to } x_2 = \int_{x_1}^{x_2} dy$$

$$= \int_{x_1}^{x_2} \frac{dy}{dx} dx = \int_{x_1}^{x_2} m(x) \, dx$$

$$= \int_{x=0}^{x_2} dy - \int_{x=0}^{x_1} dy = \int_{x=0}^{x_2} \frac{dy}{dx} dx - \int_{x=0}^{x_1} \frac{dy}{dx} dx = \int_{x=0}^{x_2} m(x) dx - \int_{x=0}^{x_1} m(x) dx$$

$$= \int \frac{dy}{dx} dx \,|_{x=x_2} - \int \frac{dy}{dx} dx \,|_{x=x_1} = \int m(x) dx \,|_{x=x_2} - \int m(x) dx \,|_{x=x_1}$$

$$= (y(x) + c)|_{x=x_2} - (y(x) + c)|_{x=x_1}$$

$$= (y(x_2) + c) - (y(x_1) + c) = y(x_2) - y(x_1)$$

Thus, the corollary allows for us to be able to evaluate indefinite integrals, if we can find any antiderivative. Again. we have seen this before. However, the corollary assumes that the derivative is continuous in the interval x=x_1 to x=x_2. That means that the derivative is not undefined (division by zero) and does not jump during that interval. Put in simple words, this means that the derivative in that interval can be drawn without picking your pen off the paper, or drawing vertical lines with a slope of infinity. Because the corollary makes the assumption, it must be true only when the assumption is true, and there are cases where it is not true.

The Newton-Leibniz Axiom

However, adding to the corollary a restriction, that the derivative is continuous in the interval, we get a result which is always true. That means that if the derivative is continuous, we can evaluate the definite integral. This additional requirement is all that the corollary is missing to be true in all cases. This result is known as the Newton-Leibniz axiom, which is also called the second part to the fundamental theorem of calculus. It was discovered by Newton and Leibniz in the late 1600s, and set the stage for the development of the rest of the field. The reason why I did not even mention continuity until now, is because the concept is nearly never violated in basic chemistry calculations, and the condition is pretty much assumed for most basic physical sciences. And even if there is a place where we encounter an issue, at this level we just cut that interval out, because it has no physical significance. When did you ever see a ball thrown suddenly disappear and appear somewhere else? That is crazy. The main reason why nearly

Appendix A: Basic Calculus
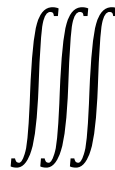
everything in the physical sciences is continuous, is because there is time, and nothing happens instantaneously. However, if we stop time, we can move the ball, and it would appear to disappear and appear somewhere else when we rewind to before the movement, and start time again. That is absurd, because time does not stop, forget about going in reverse!

Changing the Order and Limits of Integration

One thing that I did not tell you, is that when integrating, we did not have to begin at zero when evaluating the definite integral. You can actually use any k, where k is an arbitrary x value, and as long as the restriction of continuity of the derivative holds, then you may do the following:

$$\int_a^k \frac{dy}{dx}\,dx + \int_k^b \frac{dy}{dx}\,dx = \int_a^b \frac{dy}{dx}\,dx$$

You can verify this visually.

Also, you can confirm, that by moving the opposite direction along the x axis, you are doing the same as undoing what you are doing when moving in the positive direction. Thus, you will get a negative result if you reverse the limits of integration for a definite integral.

$$\int_{x_1}^{x_2} \frac{dy}{dx}\,dx = -\int_{x_2}^{x_1} \frac{dy}{dx}\,dx$$

And, it also follows, that you may do the following, if the derivative is continuous over the entire interval:

$$\int_{x_1}^{x_2} \frac{dy}{dx}\,dx = \int_k^{x_2} \frac{dy}{dx}\,dx - \int_k^{x_1} \frac{dy}{dx}\,dx \text{, where } k \text{ is any arbitrary number}$$

Because

$$-\int_k^{x_1} \frac{dy}{dx}\,dx = +\int_{x_1}^k \frac{dy}{dx}\,dx$$

And since addition is commutative, we have:

Appendix A: Basic Calculus

$$\int_{x_1}^{x_2} \frac{\mathrm{d}y}{\mathrm{d}x}\,\mathrm{d}x = \int_{k}^{x_2} \frac{\mathrm{d}y}{\mathrm{d}x}\,\mathrm{d}x - \int_{k}^{x_1} \frac{\mathrm{d}y}{\mathrm{d}x}\,\mathrm{d}x = \int_{k}^{x_2} \frac{\mathrm{d}y}{\mathrm{d}x}\,\mathrm{d}x + \int_{x_1}^{k} \frac{\mathrm{d}y}{\mathrm{d}x}\,\mathrm{d}x = \int_{x_1}^{k} \frac{\mathrm{d}y}{\mathrm{d}x}\,\mathrm{d}x + \int_{k}^{x_2} \frac{\mathrm{d}y}{\mathrm{d}x}\,\mathrm{d}x$$

Which then results in what we started with, if we combine the two integrals:

$$\int_{x_1}^{x_2} \frac{\mathrm{d}y}{\mathrm{d}x}\,\mathrm{d}x = \int_{x_1}^{x_2} \frac{\mathrm{d}y}{\mathrm{d}x}\,\mathrm{d}x$$

The Natural Exponential Function

There are numerous other derivatives and antiderivatives (integrals), but luckily, we will either use our calculator, or a table to find our results. It is a pain in the rear end to have to know all of them. In the age of the internet, it has become common practice to just look them up, and carefully step around the mathematics to get the physical results that we want. However, the mathematics is important, and there are a few special derivatives and integrals that we need to understand, because they are handy later on. However, the most important aspect is understanding and interpreting applications of basic derivatives and integrals. One such special derivative and integral is that of e^x. The integral and derivative of e^x is just e^x, and that is something good to know sometimes. The Euler's constant, which is irrational just like pi, is approximately equal to $e \approx 2.718$. It is specifically defined, so that it is its own derivative. That means that the area underneath $y = e^x$ from 0 to the x value of a point is equal to the y value of the point, which is in turn equal to the slope of the graph at that point. Repeated differentiation simply produces the same result, because we would then be differentiating the same function.

Repeated Differentiation

Explaining repeated differentiation requires looking at differentiation as an operator. Therefore, we must look at:

$$\frac{\mathrm{d}}{\mathrm{d}x}, \text{the differential operator}$$

This means that d/dx takes the derivative of whatever is written after it. Thus,

Appendix A: Basic Calculus

$$\left(\frac{d}{dx}\right)(y(x)) = \frac{d(y(x))}{dx} = m(x)$$

This is known as the first derivative of y(x). If we differentiate again, we just put another $\frac{d}{dx}$ in front of it, and differentiate whatever result, dy/dx=m(x) again. Thus,

$$\left(\frac{d}{dx}\right)\left(\frac{d}{dx}\right) = \frac{d^2}{(dx)^2}$$

$$\left(\frac{d}{dx}\right)\left(\frac{d}{dx}\right)(y(x)) = \left(\frac{d}{dx}\right)^2 (y(x)) = \left(\frac{d}{dx}\right)\left(\frac{d(y(x))}{dx}\right) = \frac{d^2}{(dx)^2}(y(x)) = \frac{d^2(y(x))}{(dx)^2}$$

Which is the second derivative. To find the third derivative, we just do the same thing, multiply another $\left(\frac{d}{dx}\right)$ in front, and call it a day. Therefore, the third derivative of y(x) is equal to $\frac{d^3 y(x)}{(dx)^3}$, and so forth.

Thus,

$$ke^x = \frac{d(ke^x)}{dx} = k\frac{d(e^x)}{dx} = \frac{d\left(k\frac{d(e^x)}{dx}\right)}{dx} = k\frac{d^2(e^x)}{(dx)^2} = \frac{d\left(k\frac{d^2(e^x)}{(dx)^2}\right)}{dx} = k\frac{d^3(e^x)}{(dx)^3}$$

and so forth

Notice how there are parentheses surrounding the dx underneath. This is because the differential operator is applied twice. However, since mathematicians have gotten used to writing in short-hand notation, in most places the parentheses are not included. Since it is easier, it is now customary to write, $\frac{d^2 y}{dx^2}$ instead of $\frac{d^2 y}{(dx)^2}$, $\frac{d^3 y}{dx^3}$ instead of $\frac{d^3 y}{(dx)^3}$, and so forth, even though the latter form is more correct, because we represent the repeated application of differential operators by raising the differential operator to a power.

And integrating, we get the same type of result:

$$\int ke^x dx = k\int e^x dx = ke^x + kc_1 = ke^x + c_2$$

We can replace kc_1 by c_2, where $c_2 = kc_1$. However, we do not even need to state that, because we do not even know what the c's are equal to, because we do not know the value of c

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Appendix A: Basic Calculus

nor k. In fact, if we do not know nor need to know any of the constants, it is even better if we do not write $c_2 = kc_1$. Because what if k is equal to zero? Then, if we make a mistake, and try to find c_1, we get $c_1 = c_2/k$, because we are assuming that k is not equal to zero. That only happens if we solve for the k incorrectly, and find a nonzero value for ke^x as well. Thus, sometimes, omission is better, if nothing else is asked for you. Integrating again, results in:

$$\int (ke^x + kc_1)dx = \int (ke^x + c_2)dx$$

$$= \int ke^x dx + \int kc_1 dx = \int ke^x dx + \int c_2 dx$$

$$= ke^x + kc_3 + kc_1 x + kc_4 = ke^x + c_2 x + k(c_3 + c_4) = ke^x + c_2 x + c_5 = ke^x + c_6 x + c_7$$

and so forth

Thus, we find that if we do not know the constant, it is just very easy to save us a lot of trouble, and replace it with c_n, where n is the next unused number! The only place where we keep the k is on the terms that we did not generate by integrating, which is ke^x in this case. Note, that differentiating as many times as integrating returns to us to e^x all over again, because one type of term, the constant term, disappears every time you differentiate.

$$\frac{d(ke^x + c_{50}x + c_{9000})}{dx} = e^x + c_{50}, \frac{d(e^x + c_{50})}{dx} = e^x$$

See that we don't even need to go in order when numbering the constants, as long as the constant with the same number is not used somewhere else. So, it is recommended that you stay in order, so that you do not repeat constants. And, if you get lost, just add a relatively large enough number to n, slap it under, and you are good to go! However, whoever is reading your work will be confused where the constants in between went.

Derivatives of Inverse Functions

Now for the derivative of an inverse function theorem, which allows us to find the next special derivative! Do you remember that the derivative power rule cannot produce anything of the form cx^{-1}? Also, do you remember that the integral power rule is invalid for cx^{-1}? Thus, we need to find the function that produces cx^{-1} when differentiated. To do so, we use the derivative

Appendix A: Basic Calculus

of an inverse function theorem. This theorem holds for functions that have an inverse. We know that the inverse of the natural exponential, e^x is $\ln(x)$. So, using the derivative of an inverse function theorem, we are going to prove that the derivative of $\ln(x)$ is equal to x^{-1}, and the integral of x^{-1} is $\ln(x)$.

The derivative of an inverse function theorem is written as follows:

$$\frac{d\left(inv(y(x))\right)}{dx} = \frac{dx}{d(y(x))}, \text{ where } inv(y(x)) \text{ is the inverse of } y(x), \text{ which is } f(y) = x$$

Substituting in the $inv(y(x))=f(y)=x$ into the y(x) on the right side, we get the following:

$$\frac{d\left(inv(y(x))\right)}{dx} = \frac{dx}{d\left(y(inv(y))\right)} = \frac{1}{\frac{d(y(x))}{dx}}$$

Now this might look hard, but the concept of it is easy. When simplified, it just looks like:

$$\frac{dy}{dx} = \frac{1}{dx/dy}$$

Why Does the Derivative of an Inverse Function Rule Work?
Now, down to why it works. When we find the inverse of a function, the graph of the inverse of the function is the graph of the original function reflected over y=x. So, since we want the derivative of the natural logarithm, we begin with its inverse, the natural exponential function. To quickly verify that the natural exponential is the inverse of the natural logarithm, below is a graph of the natural exponential, a graph of y=x, and a graph of the natural exponential that has been reflected over the line y=x. We see indeed, that reflecting the natural exponential over the line y=x results in the natural logarithm, which confirms that they are inverses of each other.

Appendix A: Basic Calculus
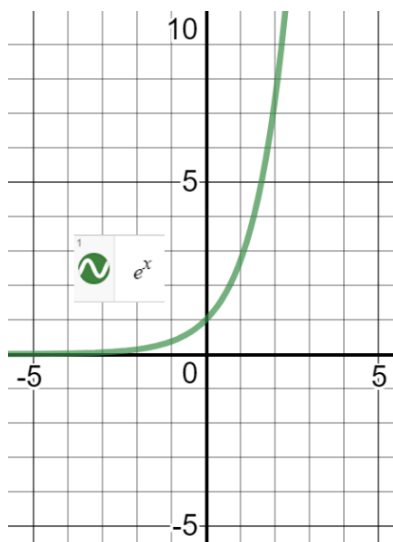
Figure A.5. The graph of y=e^x.
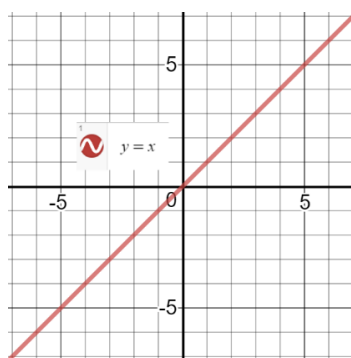
Figure A.6. The graph of y=x.
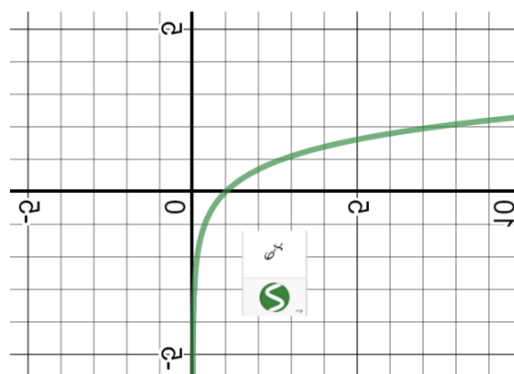
Figure A.7. When the graph of y=e^x is reflected over the line y=x, we get the same graph as the natural logarithm. Thus, the inverse of the natural exponential is the natural logarithm, which allows for us to find a special derivative and a corresponding special integral.

Appendix A: Basic Calculus
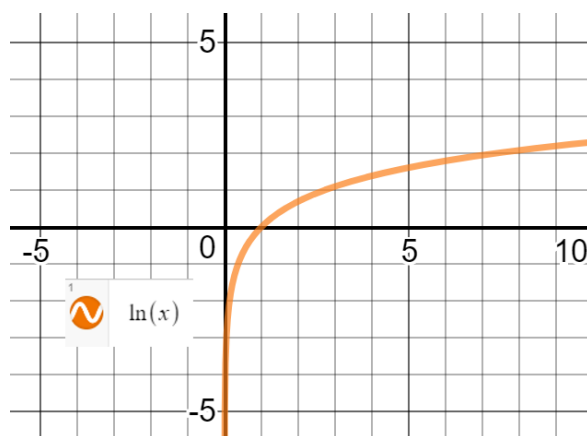
Figure A.8. The graph of y=ln(x), which is the inverse of y=e^x.

We graph (x,y) on the horizontal and the vertical axes for the original function. Since the inverse function reverses the original function, we can graph the inverse function by graphing the (y,x) of the original function onto the vertical and horizontal axes. From our slope formula, we find that doing the slope formula on a corresponding interval on the inverse function gives us the inverse of the slope that we found for the original interval on the original function. Thus, in the case of y(x)=mx+b, a line with a constant slope, we can demonstrate the principle.

$$y(x) = mx + b, \text{ so } inv\big(y(x)\big) = x(y) = \frac{y - b}{m} = \frac{y}{m} - \frac{b}{m}$$

Note how switching the variables, we found the inverse. Since the x values of the original are the y values of the inverse, and the y values of the original are the x values of the inverse, we find that the slope for a corresponding interval is always the inverse. When we apply our limit definition of a derivative, we get the same thing:

$$\frac{d(y(x))}{dx} = \lim_{\Delta x \to 0} \frac{y(x + \Delta x) - y(x)}{\Delta x}$$

Thus

$$\frac{d(x(y))}{dy} = \lim_{\Delta y \to 0} \frac{x(y + \Delta y) - x(y)}{\Delta y}$$

Appendix A: Basic Calculus

Because of the reversal of roles, if you reorganize it, you simply get our inverse function theorem, which is:

$$\frac{d\big(x(y)\big)}{dy} = \frac{1}{\dfrac{d\big(y(inv(y(x)))\big)}{dx}} = \frac{1}{\dfrac{d(y[x(y)])}{d(x(y))}} = \frac{1}{\dfrac{d(y(x))}{dx}}$$

Note how we can substitute in x(y)=*inv*(y(x))=x. That is important, and just changes the variables, which makes the equation useful. Thus, the formula does the following. For a function, the x(y)=inv(y(x)) does the inverse of y, and finds the corresponding point, where the derivative of the original function is equal to the inverse of the derivative of the inverse function. Then, it uses the derivative of the original function to find the inverse of the derivative of the inverse function at the corresponding point. Doing the inverse results in the derivative of the corresponding point that we wanted. Notice that when y=x, the derivative of the inverse function is the same as the derivative of the original, because the inverse of y=x is simply y=x. The same holds, for y=x+c, where the inverse is simply x=y-c. Thus, any function of the form y=x+c where c is some constant results in lines that are parallel to y=x. Reflecting over parallel lines does not change the slope of a line, and therefore we will get the same constant slope, 1, which is equal to the derivative of that line. Now, knowing how the derivative of an inverse function theorem works, we can use the fact that inverse of y=e^x is equal to $\log_e(y)=\ln(y)$. Now, we can get to work proving the derivative of a natural logarithm, and the integral of an inverse.

The Derivative of the Natural Logarithm, and the Integral of 1/x

$$inv\big(y(x)\big) = x(y) = inv(e^x) = \log_e(y) = \ln(y)$$

$$\frac{d\big(x(y)\big)}{dy} = \frac{1}{\dfrac{d(y(x))}{dx}} = \frac{1}{\dfrac{d(y[x(y)])}{d(x(y))}} = \frac{1}{\dfrac{d\big(y(inv(y(x)))\big)}{dx}}$$

Note that substituting in the y(x) for the equation equal to the original results in the equation of

$$\frac{1}{\text{derivative of orignal function for a given x on the original function}}.$$ That is the slope of the corresponding point on the inverse. If we know the vertical axis value of the inverse, (x, because we switch the

Appendix A: Basic Calculus

two variables when we invert functions), we can find the slope of the inverse that has that vertical axis value. However, since we switched the variables, the derivative we want preferably involves a y value, because that is the horizontal axis value. So, we substitute further, and get the preferred formula. I'll tell you why it is preferred.

$$\frac{d(\ln(y))}{dy} = \frac{1}{\frac{d(e^x)}{dx}} = \frac{1}{\frac{d(e^{\ln(y)})}{d(\ln(y))}} = \frac{1}{\frac{d(y[x(y)])}{d(x(y))}} = \frac{1}{\frac{d\left(y(inv(y(x)))\right)}{dx}}$$

Following from what we had before, the derivative of e to the something is e to that something times a constant. Thus, in the case where we have y, the coefficient in front of y is 1, because the coefficient of its inverse, e^x, has an unwritten coefficient of 1. Thus, we can continue simplifying

$$= \frac{1}{\frac{d(e^{\ln(y)})}{d(\ln(y))}} = \frac{1}{e^{\ln(y)}}$$

Since performing the inverse of a function on the function returns the original value,

$$e^{\ln(y)} = y$$

And, we complete the proof, that

$$\frac{d(\ln(y))}{dy} = \frac{1}{y}$$

Now, we can redefine the variables of an inverse function so that the x values correspond to the y values of the original, and the y values correspond to the x values of the original, and plot it as (x,y). In fact, in the formula above, we can substitute any variable, t, x, a, d, etc for the y. Thus, we use x, because that is what we are most comfortable using at this point, I believe. So:

$$\frac{d(\ln(x))}{dx} = \frac{1}{x}$$

And since integration is just antidifferentiation, the integral of the inverse of x is just the natural logarithm of x plus a constant, for all positive values of x.

$$\int \frac{1}{x} dx = \ln(x) + c \text{ for all positive values of } x$$

Appendix A: Basic Calculus
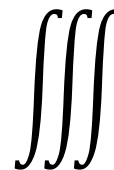
Note that the natural logarithm is not defined for $x \leq 0$. Also note that e^x likewise has no negative y values. Thus, we run into a problem, when we go to the negative numbers, and cross the vertical line x=0. Since the natural logarithm is undefined for negative x values, we will never need to find the value nor the derivative of the natural logarithm for negative x values. However, what we may be asked to do, is to find the integral of 1/x, when the x values are negative. Noting that 1/x for negative x values is just the graph of 1/x for positive x values reflected over y=-x. Thus, again, going back to the integral, we have:

$$\int \frac{1}{x} dx = \ln|x| + c \text{ for all } x \text{ values}$$

Thus, this allows us to find the area between 1/x and the x axis and two vertical lines, x=x_1

And x=x_2, with both vertical lines being equal to negative values of x. Because of physical constraints, we will never need to integrate through zero at this level, because 1/x is not continuous at x=0 due to 1/0, which is a vertical asymptote. We will not need to deal with that problem!

Other Special Integrals and Derivatives

Other special integrals and derivatives are provided below. Their proofs are quite long, but a simple google search should bring up the proofs.

$$\frac{d[\ln(x)]}{dx} = \frac{1}{x}, and \int \frac{1}{x} dx = \ln|x| + c$$

$$\frac{d[\sin(x)]}{dx} = \cos(x), \frac{d[\cos(x)]}{dx} = -\sin(x), \frac{d[-\sin(x)]}{dx} = -\cos(x), \frac{d[-\cos(x)]}{dx} = \sin(x)$$

And that's about it, for the basics!

A Little Bit About Partial Derivatives

Sometimes, we want to find the change of a variable that happens if we change another variable. Often, all other variables are kept constant. We call this the partial differential of the variable. If only two variables change, and one depends on the other, we can differentiate a given

Appendix A: Basic Calculus

equation, and keep all other variables constant. The partial differential symbol, ∂, means that we are changing the variable that follows it by a very small amount. Thus, we can differentiate the equation:

$$y = 3xz + z^2x^5 + 2$$

Which can result in:

$$\left(\frac{\partial y}{\partial x}\right)_z = 3z + 5z^2x^4$$

Or:

$$\frac{\partial y}{\partial z} = 3x + 2zx^5,\ \text{x constant}$$

I wrote them in two different ways, to show two separate notations that indicate the constant variable. In the first case, what is next to the ∂ changes, and the subscript z means that z is held constant. In the second case, still what is next to the ∂ changes, but x is held constant, as stated. This is important, as it keeps track of the other variables in the system.

Which equation we result in depends on which relation we are interested in investigating. These are not quite useful for obtaining empirical relations, if there are more than two variables changing, or if the two variables changing are not related to one another. There is not much to say, as they generally obey the same rules that the previous types of derivatives follow. Partial derivatives are mainly used when we look at thermodynamics, gases, and reaction kinetics. I will try to avoid them as much as possible, because most topics pertaining to partial derivatives are out of the scope of the text, with the exception of heat capacities.

Appendix A: Basic Calculus

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Detailed Table of Contents

Detailed Table of Contents

Detailed Table of Contents

Detailed Table of Contents

Detailed Table of Contents

318

Detailed Table of Contents

Detailed Table of Contents

Detailed Table of Contents

Chapter 9: Kinetics and Equilibrium Derivations 261

Appendix A: Basic Calculus...271

Detailed Table of Contents

The Periodic Table

Legend:

atomic number — 6
symbol — C
name — carbon
atomic mass — 12.011
common oxidation states — -4, +2, +4

☐ metals ☐ metalloids ☐ nonmetals ☐ unknown

1 — group IUPAC
1A — group CAS

Main groups (period 1–7):

Period	1 / 1A	2 / IIA	13 / IIIA	14 / IVA	15 / VA	16 / VIA	17 / VIIA	18 / VIIIA
1	1 H hydrogen 1.0079 (+1, -1)							2 He helium 4.0026
2	3 Li lithium 6.941 (+1)	4 Be beryllium 9.012 (+2)	5 B boron 10.811 (+3)	6 C carbon 12.011 (-4, +2, +4)	7 N nitrogen 14.007 (-3, +1, +2, +3, +4, +5)	8 O oxygen 15.999 (-2)	9 F fluorine 18.998 (-1)	10 Ne neon 20.179
3	11 Na sodium 22.990 (+1)	12 Mg magnesium 24.305 (+2)	13 Al aluminum 26.982 (+3)	14 Si silicon 28.086 (-4, +4)	15 P phosphorus 30.976 (-3, +3, +5)	16 S sulfur 32.065 (-2, +4, +6)	17 Cl chlorine 35.453 (-1, +1, +3, +5, +7)	18 Ar argon 39.948
4	19 K potassium 39.098 (+1)	20 Ca calcium 40.078 (+2)	31 Ga gallium 69.723 (+3)	32 Ge germanium 72.64 (-4, +4)	33 As arsenic 74.922 (-3, +3, +5)	34 Se selenium 78.96 (-2, +4, +6)	35 Br bromine 79.904 (-1, +1, +5)	36 Kr krypton 83.798 (+2, +4)
5	37 Rb rubidium 85.468 (+1)	38 Sr strontium 87.62 (+2)	49 In indium 114.818 (+3)	50 Sn tin 118.710 (+2, +4)	51 Sb antimony 121.760 (-3, +3, +5)	52 Te tellurium 127.60 (-2, +4, +6)	53 I iodine 126.904 (-1, +1, +5, +7)	54 Xe xenon 131.293 (+2, +4, +6)
6	55 Cs cesium 132.905 (+1)	56 Ba barium 137.327 (+2)	81 Tl thallium 204.383 (+1, +3)	82 Pb lead 207.2 (+2, +4)	83 Bi bismuth 208.980 (+3, +5)	84 Po polonium (210) (+2, +4)	85 At astatine (210) (-1)	86 Rn radon (220)
7	87 Fr francium (223) (+1)	88 Ra radium (226) (+2)	113 Nh nihonium (286)	114 Fl flerovium (289)	115 Mc moscovium (289)	116 Lv livermorium (293)	117 Ts tennessine (294)	118 Og oganesson (294)

Transition metals (groups 3–12):

Period	3 / IIIB	4 / IVB	5 / VB	6 / VIB	7 / VIIB	8 / VIIIB	9 / VIIIB	10 / VIIIB	11 / IB	12 / IIB
4	21 Sc scandium 44.956 (+3)	22 Ti titanium 47.867 (+2, +3, +4)	23 V vanadium 50.942 (+2, +3, +4, +5)	24 Cr chromium 51.996 (+2, +3, +6)	25 Mn manganese 54.938 (+2, +3, +4, +6, +7)	26 Fe iron 55.845 (+2, +3)	27 Co cobalt 58.933 (+2, +3)	28 Ni nickel 58.693 (+2, +3)	29 Cu copper 63.546 (+1, +2)	30 Zn zinc 65.38 (+2)
5	39 Y yttrium 88.906 (+3)	40 Zr zirconium 91.224 (+4)	41 Nb niobium 92.906 (+3, +5)	42 Mo molybdenum 95.96 (+4, +6)	43 Tc technetium (98) (+4, +6, +7)	44 Ru ruthenium 101.07 (+3, +4, +8)	45 Rh rhodium 102.91 (+3)	46 Pd palladium 106.42 (+2, +4)	47 Ag silver 107.87 (+1)	48 Cd cadmium 112.441 (+2)
6	71 Lu lutetium 174.97 (+3)	72 Hf hafnium 178.49 (+4)	73 Ta tantalum 180.948 (+5)	74 W tungsten 183.84 (+6)	75 Re rhenium 186.207 (+4, +6, +7)	76 Os osmium 190.23 (+3, +4, +6, +8)	77 Ir iridium 192.217 (+3, +4)	78 Pt platinum 195.084 (+2, +4)	79 Au gold 196.967 (+1, +3)	80 Hg mercury 200.59 (+1, +2)
7	103 Lr lawrencium (262) (+3)	104 Rf rutherfordium (261) (+4)	105 Db dubnium (262)	106 Sg seaborgium (266)	107 Bh bohrium (264)	108 Hs hassium (277)	109 Mt meitnerium (268)	110 Ds darmstadtium (271)	111 Rg roentgenium (272)	112 Cn copernicium (285)

Lanthanides:

57 La lanthanum 138.905 (+3)	58 Ce cerium 140.116 (+3, +4)	59 Pr praseodymium 140.908 (+3)	60 Nd neodymium 144.242 (+3)	61 Pm promethium (145) (+3)	62 Sm samarium 150.36 (+2, +3)	63 Eu europium 151.964 (+2, +3)	64 Gd gadolinium 157.25 (+3)	65 Tb terbium 158.925 (+3)	66 Dy dysprosium 162.500 (+3)	67 Ho holmium 164.930 (+3)	68 Er erbium 167.259 (+3)	69 Tm thulium 168.934 (+3)	70 Yb ytterbium 173.054 (+2, +3)

Actinides:

89 Ac actinium (227) (+3)	90 Th thorium 232.038 (+4)	91 Pa protactinium 231.036 (+4, +5)	92 U uranium 238.029 (+3, +4, +5, +6)	93 Np neptunium (237) (+3, +4, +5, +6)	94 Pu plutonium (244) (+3, +4, +5, +6)	95 Am americium (243) (+3, +4, +5, +6)	96 Cm curium (247) (+3)	97 Bk berkelium (247) (+3, +4)	98 Cf californium (251) (+3)	99 Es einsteinium (252) (+3)	100 Fm fermium (257) (+3)	101 Md mendelevium (258) (+2, +3)	102 No nobelium (259) (+2, +3)